UNSATURATED ORGANOSILICON POLYMERS VIA ACYCLIC DIENE METATHESIS (ADMET) CONDENSATION POLYMERIZATION

By

DENNIS W. SMITH, JR.

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This dissertation is dedicated to my mother,

Margaret McCurdy Saunders

for her integrity and unrelentless intoleration for anything but my very best.

-YAMPIAYF

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Abstract of Dissertation Presented to the Graduate School
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UNSATURATED ORGANOSILICON POLYMERS
VIA ACYCLIC DIENE METATHESIS
(ADMET)
CONDENSATION POLYMERIZATION

By
Dennis W. Smith, Jr.

December 1992

Chairman: Professor Kenneth B. Wagener
Major Department: Chemistry

The design and synthesis of unsaturated organosilicon polymers prepared via acyclic diene metathesis (ADMET) condensation polymerization is presented. ADMET polymerization constitutes a new equilibrium step condensation type polymerization where the production and removal of a small alkene condensate drives the reaction. Well defined high molecular weight polymers with known alkene end groups result from ADMET, which is only possible when Lewis acid free metathesis alkylidenes of the type, $M{=}CHR(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$ (M = W or Mo), are employed as catalysts.

Various carbosiladienes and carbosiloxadienes were designed and synthesized in order to ascertain the specific monomer structural requirements dictated by this polymerization method. Vinylsilane monomers do not homopolymerize due to steric inhibition within a required catalytic intermediate, yet will specifically copolymerize with an unhindered diene resulting in isolated

units of the vinyl silane within the copolymer. Allylic silanes show no resistance to homometathesis and afford novel high molecular weight unsaturated polycarbosilanes with low glass transition temperatures and good thermal stability.

Bis(allyl)tetramethyldisiloxane underwent quantitative cyclization when treated with the molybdenum alkylidene giving the 7-membered cyclosiloxalkene. Cyclization is avoided if the monomer is designed so as to kinetically disfavor the cyclized product. An extension of the methylene groups between the olefin and the siloxane linkage or extension of the siloxane linkage results in facile polymerization to new high molecular weight unsaturated polycarbosiloxanes with low glass transition temperatures and good thermal stability. Hydrosilation oligomerization was used to synthesize an α,ω-telechelic diene macromonomer which underwent clean ADMET polymerization to high molecular weight.

In some cases, cyclic products are observed at the end of the polymerizations due to a kinetically slow back biting mechanism when cyclic products are favored. Cyclic products are only observed at the end of the polymerizations where a postcondensation resting state had been established involving ring/chain equilibria. Back biting reactions can be enhanced by removal of the cyclic byproduct in the bulk or, to a greater extent, by diluting active polymer.

A discriminate co-condensation between a well defined unsaturated polycarbosiloxane oligomer and an aromatic diene monomer was also demonstrated. The controlled solution addition of an aromatic diene to an existing polymer resulted in continued polycondensation to a high molecular weight copolymer containing isolated units of the aromatic diene.

Complete synthesis, characterization and behavior are discussed for these new organosilicon polymers.

CHAPTER 1

INTRODUCTION

> Dear Colleague, Leave the concept of large molecules well alone...There can be no such thing as a macromolecule.
>
> --*Advice given to Hermann Staudinger in 1920*[1]

Nobel Laureate Hermann Staudinger forged the foundation of modern polymer chemistry during the 1920s when he established that natural and synthetic polymers were not colloidal aggregates of small molecules but were long molecular chains with characteristic terminal groups. These observations were the beginnings of answers but certainly not of questions, since as early as 1839, Charles Goodyear demonstrated the vulcanization of rubber.[2] From that time forward, chemists have explored every discipline of the natural sciences discovering, defining, and exploiting the vastness of macromolecules. Today, a great many chemists and chemical engineers are involved with some facet of polymer science or technology, the breadth of which affects us all. For these beginnings it must be acknowledged that all of macromolecular science is dedicated to the appreciation of those concepts developed by Staudinger, Carothers, Mark, Flory, Butler, Marvel, and other leaders of their day.[1-8]

This dissertation details the development of acyclic diene metathesis (ADMET) polymerization as applied to silicon containing dienes. The monomer structural requirements for, and the synthesis, characterization, and behavior of novel unsaturated organosilicon polymers is presented. This chapter introduces pertinent aspects of organosilicon chemistry, and organosilicon polymer

chemistry, as well as a historical development of olefin metathesis leading to metathesis condensation polymerization. An instructive background and literature review is necessary for a complete appreciation of the chemistry described herein.

History and Fundamentals of Organosilicon Chemistry

No naturally occurring organosilanes exist. Organosilicon compounds were first reported in 1863 when Friedel and Crafts[9] prepared tetraethylsilane from diethylzinc and tetrachlorosilane, thereby presenting the first compound of its kind. Fredrick S. Kipping[10] began the first systematic study of organosilanes in 1898 for which he is deservingly referred to as, "the father of organosilicon chemistry." Kipping's fundamental work in organosilicon chemistry was soon transformed into an unique foundation; for unlike the history of most classes of compounds, the true development of organosilanes was founded in polymer chemistry with the advent of silicone polymers in the 1940's[11,12] which provided the thrust of their exploration. Today, organosilicon chemistry is present in a vast number of applications ranging from synthetic reagents and intermediates,[13-16] bioactive molecules,[17] biomedical materials,[18] electronic devices,[19] specialty plastics,[18] elastomers,[18,20] coatings,[19] and fibers.[19,20]

Although silicon is similar, chemically, to carbon in many ways, its resistance to form multiple bonds as carbon does has been an area of productive research. Compounds such as stable disilenes, Si=Si,[21-24] are currently being studied as well as other unsaturated silicon compounds of the type Si=X, where X = C,[26] N,[25] and O.[25] These are highly reactive molecules and polymerize or cyclodimerize instantaneously if not structured with sufficient bulk.[21,25,26]

As a second row group IV element beneath carbon, silicon shares its most common quadricovalency with its neighbor. However, unlike carbon, silicon

possesses the ability to expand or contract its covalency to accommodate, reportedly, coordination numbers ranging from 1 to 10.[27] A comparison of some atomic parameters between carbon and silicon (Table 1.1 and 1.2)[28,29] is illustrative of silicon's unique reaction chemistry where frequently it is viewed as a selective replacement for H in the C-H bond.[28]

Table 1.1. Atomic parameters of carbon and silicon.

Physical Parameter	Carbon	Silicon
atomic radius	0.66 Å	1.06 Å
covalent radius	0.77 Å	1.17 Å
electronegativity	2.5 (Pauling)	1.8 (Pauling)
1st ionization potential	259.0 (kcal/mol)	187.9 (kcal/mol)

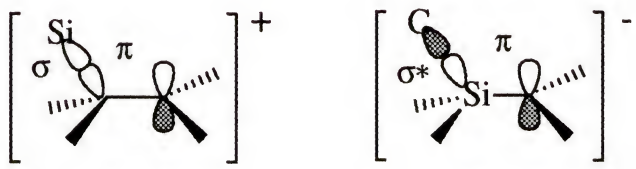
Table 1.2. Selected bond dissociation energies and bond distances of carbon and silicon.

Si-X bond	Si-X energy (kJ/mol)	Si-X distance (Å)	C-X bond	C-X energy (kJ/mol)	C-X distance (Å)
Si-C	318	1.89	C-C	334	1.54
Si-O	531	1.63	C-O	340	1.31
Si-Cl	471	2.05	C-Cl	335	1.78
Si-F	808	1.60	C-F	452	1.39

As illustrated in tables 1.1 and 1.2, silicon is larger than carbon and makes strong bonds to oxygen and the halogens. The halogen silicon bond is perhaps the most versatile and well exploited aspect of organosilicon chemistry. Although Si-X bonds are homolytically strong, they easily undergo heterolytic cleavage under kinetically favored conditions. However, the most effective difference between silicon and carbon is silicon's low electronegativity which is even below that for hydrogen. This property is most important since the polarity of the C-Si bond is

greater than that of the C-H bond. For example, nucleophiles will selectively attack silicon and favor substitution over competing proton/base reactions.[15]

This polarization also accounts for the well known β-effect and α-anion stabilization prevalent in organosilicon chemistry (Figure 1.1).[14,28] The β-effect refers to the carbocation stabilization derived from a β silicon atom and has been ascribed to (σ-p)π overlap of the C-Si σ bond with an adjacent empty p-orbital. Due to this polarization, a higher coefficient of electron density is found on carbon which stabilizes the cation through hyperconjugation. Similarly, the electropositve aspect of silicon provides stabilization to an α-anion, through hyperconjugation with an adjacent Si-C σ* orbital which more closely matches the energy of the anion.



(σ-p)π
β-effect

(σ*-p)π
α-anions

Figure 1.1. The β-effect and α-anion stabilization.

Examples of the β-effect are most clearly demonstrated from well known electrophilic substitutions of organosilanes, such as the use of allyl silanes as allylation reagents which pass through a β-silicon stabilized carbocation.[15] The α-anion effect is commonly found where good carbon electrophiles α to silicon are desired, or where stabilized α-silyl anions are used. In any case, both of these effects are of tremendous value to the synthetic organic chemist as evident by the wide variety of protecting groups[16] and synthetic reagents[29] derived from organosilanes. However, despite these uses for organosilicon compounds in

organic chemistry, arguably the greatest impact of organosilane chemistry is most clearly demonstrated when applied to macromolecules.

Current Scope of Silicon Based Polymer Chemistry

Few elements in the periodic chart have eluded macromolecular representation in some form. Although carbon based molecules and their common construction with heteroatoms such as oxygen, nitrogen, sulfur, and the halogens comprise the majority of known macromolecules, the synthesis and study of well defined inorganic and organometallic polymers is currently experiencing a renaissance due to the vast array of unique properties they possess.[17-21]

Polymers containing various organosilicon functionalities have, for decades, led the field of hybrid polymer development. The chemical and physical diversity of silicon provides the polymer chemist with exceptional variation of structure and properties second only to carbon.[20] Of the many and exotic varieties of hybrid polymers containing silicon, the most important to date include polysiloxanes (silicones), polycarbosiloxanes, polysilanes, and polycarbosilanes; each of which is briefly introduced here.

Considerable emphasis has been devoted to the synthesis and study of organosiloxane polymers due to their unique combination of properties, including low temperature flexibility, hydrophobicity, and good thermal stability.[11,20,30] In addition, organosiloxane polymers exhibit excellent radiation and oxidative resistance, biocompatability, and high gas permeability.[19]

Polysiloxanes or silicones are organosubstituted polymers containing an alternating silicon/oxygen backbone, of which the hydroxy terminated poly(dimethylsiloxane), $HO\text{-}(Me_2Si\text{-}O)_n\text{-}H$, was the first observed, by Kipping,[10] in 1930. While attempting to prepare the silicon analog of ketones, Kipping

obtained "undesirable oils," and being aware of Staudinger's previous (since 1920) and concurrent work delineating the founding concepts of macromolecules, he rationalized their formation as linear siloxane polymers and declared them "silicones."[10]

Polysiloxanes are prepared by a variety of methods, yet by far, most siloxane products originate from halo-substituted organosilane precursors. The direct production of halo-substituted organosilanes from the copper catalyzed thermolysis of elemental silicon and alkylhalides was developed by Eugene Rochow,[31,32] which became commercial in 1941, and is referred to as the Rochow process still today (Figure 1.2).

$$RX + Si \xrightarrow[\Delta]{[Cu]} R_{4-n}SiX_n$$

Figure 1.2. Synthesis of organohalosilanes via the Rochow process.

Polysiloxanes also are formed upon the direct hydrolysis of dihalodialkylsilanes or dialkoxydialkylsilanes, yet the condensation polymerization is low yielding and gives predominantly the favored cyclic tri, tetra, and higher siloxanes.[29] These cyclic siloxanes, themselves, are most effectively used as monomers in ring opening polymerizations initiated by a variety of acidic (Lewis or protic), basic (typically hydroxide), or nucleophilic (organometallic salts) initiators.[33] Mixtures of initiator, cyclic siloxanes, catalyst, and end-cappers undergo equilibrium polymerization by heating under varied conditions to produce linear and cyclic polysiloxanes (Figure 1.3).[33]

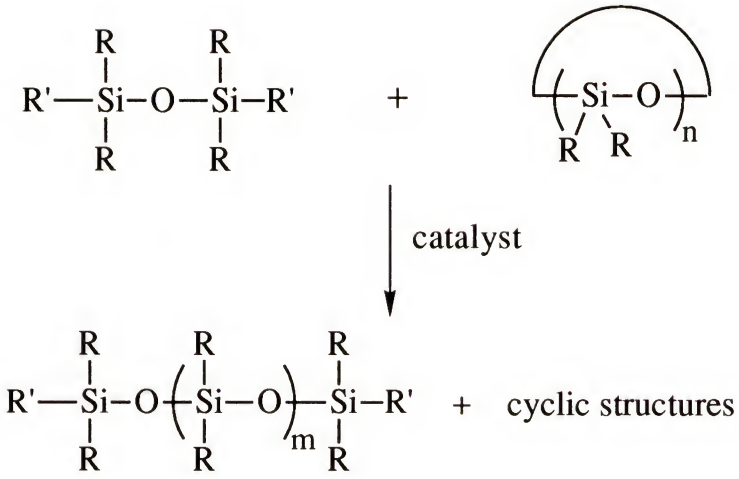


Figure 1.3. Synthesis of Polysiloxanes (n = 3 or 4).

A variety of pendant groups (R in Figure 1.3), including phenyl, vinyl, and hydrogen are commonly used and dictate the specific properties desired. Reactive groups along the polymer chain serve as branching points during cross linking (or curing) in the production of silicone elastomers.[20] Polysiloxanes can also be terminated with a variety of groups (R' in Figure 1.3). Unreactive silicone oils and resins are obtained when R' is alkyl or phenyl, yet reactive terminal groups such as hydroxy (silanol), amine, or hydrogen provide access to valuable telechelic (α,ω-difunctional) polymers.[18,20,34]

Telechelic siloxane polymers can undergo chain extension polymerization to give a variety of hybrid systems where siloxane incorporation into the polymer main chain is used to tailor specific properties.[34] In particular, much effort has been devoted to the synthesis of poly(imidosiloxanes)[35,36] which are targeted for a variety of specialty applications. Block copolymers of poly(dimethylsiloxane) and a variety of polyolefins, polycarbonates, and polyoxyalkylenes which, for example, find application as polymer blend compatibilizers, have also been prepared.[37] Whatever their use, all polysiloxanes attribute their attractive properties to the strength, length, and flexibility of the Si-O bond (Table 1.1 and

1.2) over extreme use temperature ranges (ca. -150° to 450° C).[38] For this reason and due to the unique hydrophobic and chemically resistant organic "shroud" provided by the alkyl substituents, organosiloxane polymers are placed in an exclusive class unvisited by any other material.

Of tremendous recent importance are siloxane networks produced from the hydrolysis of tetraalkoxysilanes. These "sol-gel"[39-42] materials comprise a unique type of synthetic silicate, $(SiO_2)_n$, which is used as precursors for high purity glasses, ceramics, coatings, and fibers.[39-41] The resulting networks exhibit a diverse range of physical properties depending on reaction and processing conditions.[41] Most recently, Shea and Webster,[42] used the sol-gel technique to construct aromatic hybrids of these inorganic networks. Organic hybrids in these systems also play an important role in dictating the morphology and thus properties of the materials.

Interesting and rare hybrids of siloxane polymers include polycarbosiloxanes which have not experienced the rapid development characteristic of siloxane systems due to synthetic difficulties. Polycarbosiloxanes possess real potential as valuable materials and are pertinent to the research detailed in later chapters of this dissertation.

Polymers possessing regularly alternating carbon and siloxane linkages within the main chain have long been desired, since the introduction of organic segments generally increases thermal stability and may improve mechanical performance of subsequent elastomers, without sacrificing advantageous siloxane properties.[38,43] The synthesis of these polycarbosiloxane systems currently is confined to the poly(silarylene-*co*-siloxanes),[38,43-47] typically prepared by the condensation of difunctionalized silanes and disilanolbenzenes (Figure 1.4), and to a limited number of saturated polycarbosiloxanes prepared by the ring opening polymerization of cyclocarbosiloxanes (Figure 1.5).[46-48] To date there have been

no reports of synthetic routes to main chain unsaturated (excluding aromatic) polycarbosiloxanes other than the results detailed in chapter four of this dissertation.

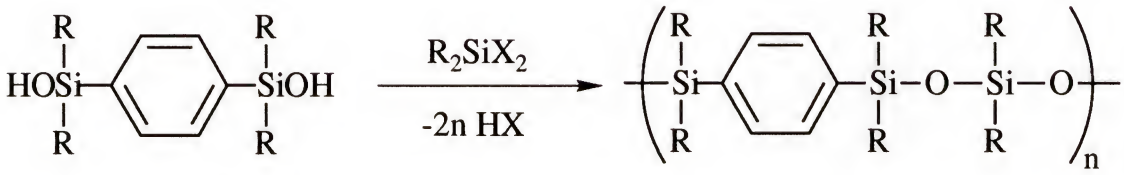


Figure 1.4. Synthesis of Silarylene-siloxane copolymers (X = halo, acetoxy, or dialkylamino groups).

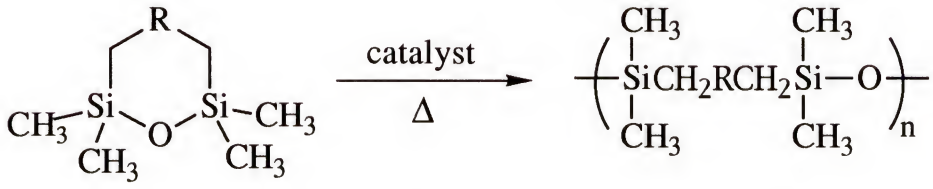


Figure 1.5. Synthesis of polycarbosiloxanes (R = 0 or 1 unsubstituted or alkyl, phenyl substituted methylene).

The versatility of the silicon atom expressed in polymer science is not only confined to its applications found when bonded to oxygen, as exhibited by the creation of an entire field of polymer chemistry based on the Si-Si bond. Organopolysilanes (or IUPAC designated polysilylenes) are linear catenated silicon polymers containing organic substituents, and are currently the topic of active research.[49] These unique polymers consisting of a purely σ-bonded Si backbone present silicon as one of the few elements, like carbon, which form stable linear macromolecules with itself.

The first reports of the preparation and characterization of organopolysilanes appeared from Burkhard[50] in 1949 when it was found that dichlorodimethylsilane undergoes Wurtz-type coupling in the presence of sodium metal to give linear poly(dimethylsilane) (Figure 1.6). However, the polymer was described as

insoluble and infusible, and subsequent investigations of organopolysilanes were completely neglected over the next 25 years.

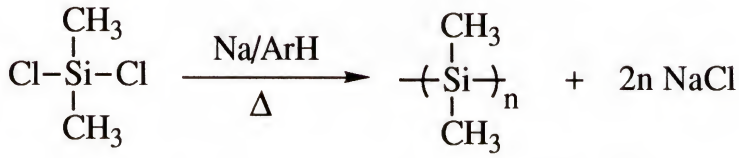


Figure 1.6. Synthesis of polysilanes via Wurtz-type coupling.

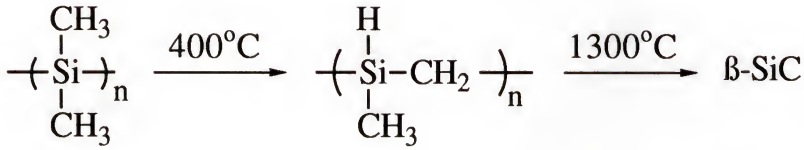


Figure 1.7. Pyrolysis of poly(dimethylsilane) to β-SiC.

The rebirth of organopolysilane research occurred in 1975 when Yajima[51] found that poly(dimethylsilane) could be used as a precursor to silicon carbide ceramics, thus providing the basis for a thriving commercial technology (Figure 1.7). This revelation stimulated an active pursuit for the preparation and properties of organopolysilanes leading to the report of West *et al.*[52] of the first soluble polymers of this type just over 10 years ago. West *et al.* discovered that the copolymerization of dichlorosilanes possessing different alkyl and aryl substituents resulted in stable high polymers which were soluble in common organic solvents.

The method of synthesizing organopolysilanes has undergone little change since Burkhard's first reports. The Wurtz-type condensation of diorganodichlorosilanes with finely divided Na in an inert solvent at temperatures above 100 °C is the preferred method of preparation for these compounds.[49,53] Recent synthetic alternatives to polysilanes include low temperature Wurtz condensation activated by ultrasound,[54] anionic ring opening polymerization of

strained cyclotetrasilanes,[55] and most recently, transition metal catalyzed dehydrogenative coupling of primary organosilanes.[56,57] The latter is proving to be quite an exceptional method, in that the mechanism of propagation has been shown to occur via a σ-bond metathesis reaction when catalyzed by various Hf or Zr metallocenes to give Si-Si bonds and H_2 as a condensation product.[57] The reaction constitutes a very rare example of condensation polymerization catalyzed by organometallic complexes. Another rare example of transition metal catalyzed metathesis chemistry is the topic of this dissertation, and is introduced in later sections.

The mechanism for the Wurtz-type condensation of dihalosilanes is complex and not fully understood. Condensation may take place on the sodium surface or in solution. Experimental evidence for both silyl radicals and silyl anions exists.[58] Whatever the exact mechanism, propagation is generally considered to be chain growth since high polymer ($M_W \sim 10^6$ in some cases) is formed at relatively low conversions despite the condensation type appearance of the reaction. However, it is generally accepted that more than one mechanism may be occurring since polysilanes prepared via Wurtz coupling typically exhibit two distinct distributions of polymer chain lengths.[53]

Currently, the most studied properties of organopolysilanes, save for their use as ceramic precursors, come from their interesting electronic spectra. A strong ultraviolet absorption due to σ-σ* excitation of the Si-Si bonding electrons is characteristic of these polymers and depends greatly upon substituent type.[59] Polyorganosilanes also exhibit a bathochromic shift as the chain length increases, as is the case for conjugated organic π-systems. These and other properties have made polysilanes the object of intense research leading to a wide variety of potential applications. Some of these include use as high resolution UV-resists in microlithography,[60] polymeric photoconductors, and charge transport media.[61]

Polysilanes can also initiate vinyl monomer polymerizations,[62] and when doped they possess semiconductor levels of conductivity[52] and have recently been shown to exhibit interesting nonlinear optical properties.[63,64]

While polysilanes were desired initially due to their ability to thermally rearrange and yield valuable silicon carbide, efforts toward synthetic routes to polycarbosilanes (the true ceramic precursor in Figure 1.7) quickly led to yet a new area of polyorganosilicon chemistry. Polycarbosilanes are broadly defined as polymers containing silicon alternating with carbon groups in the backbone.[65] A brief introduction to saturated polycarbosilanes is given followed by recent advances in the synthesis of unsaturated polycarbosilanes.

The first general route to polycarbosilanes, reported prior to Yajima's high yielding SiC process shown in Figure 1.7, was achieved via the coupling of (halomethyl)halosilanes with sodium or magnesium (Figure 1.8).[66,67] This method gave low molecular weight products in poor yields due to predominant cyclization.

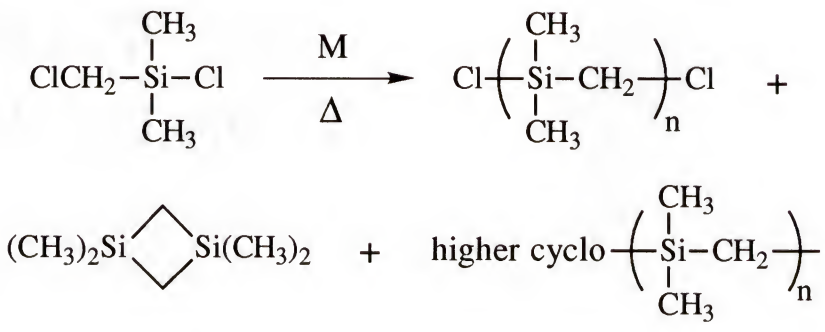


Figure 1.8. Polycarbosilane synthesis via coupling of (halomethyl)halosilanes where M = Mg or Na.

The [Pt] catalyzed hydrosilation polymerization of vinylsiliconhydrides has also been used to prepare saturated polycarbosilanes.[68-74] Hydrosilation chemistry proceeds much more cleanly than the metal coupling of halosilanes,

where β-addition predominates, as shown in Figure 1.9. More recently, a saturated polycarbosilane, similar to that represented in Figure 1.9 yet containing a Si-Si bond, has been synthesized by the electrochemical reduction of bis(chlorosilyl)ethanes.[75]

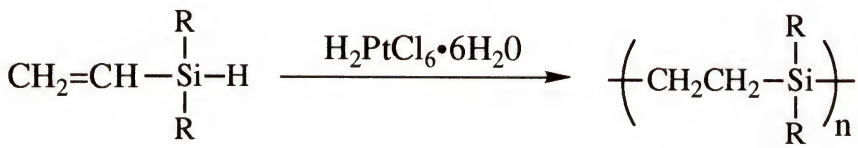
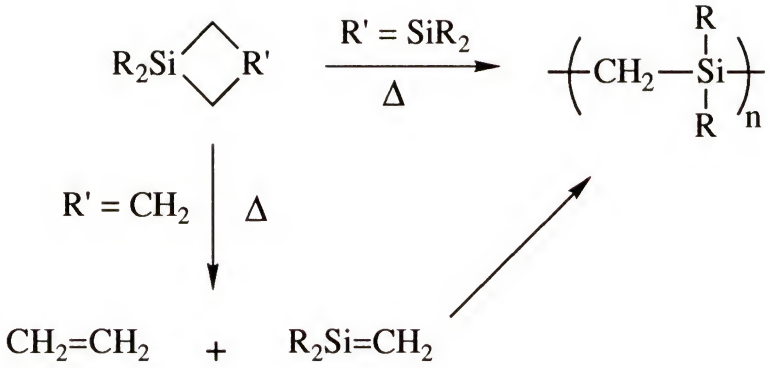


Figure 1.9. Polycarbosilane synthesis via hydrosilation polymerization (only β-adduct shown).

More useful routes to polycarbosilanes include various techniques involving the ring opening polymerization of cycloorganosilanes. Examples of thermolytic,[76] anionic,[77] and metal catalyzed[78] methods are presented in Figure 1.10. These processes are generally not well defined, and mixtures of products are usually obtained. Furthermore, unlike the Yajima polycarbosilane (Figure 1.7), most saturated polycarbosilanes of these types do not give high ceramic yields without subsequent cross linking.[65] However, very recently, the polycarbosilane represented in Figure 1.10.1 where R = H exhibited remarkably high ceramic yields (87%).[78] This polymer was obtained from the direct reduction of the same starting structure where R = Cl and was synthesized similarly as shown in Figure 1.10.1 for R' = $SiCl_2$ and R = Cl and was catalyzed by platinum-based hydrosilation type catalysts. This polycarbo(chloro)silane and its reduction were also reported earlier via the $AlCl_3$ catalyzed methyl-chlorine exchange of trimethylchlorosilane and the polycarbosilane shown in Figure 1.10.1 (R = Me).[79,80]

1.10.1) Thermolytic



1.10.2) Anionic

1.10.3) Metal catalyzed

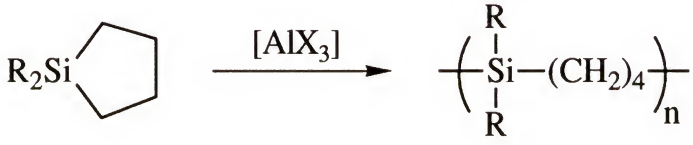


Figure 1.10. Saturated polycarbosilane synthesis via ring opening polymerization.

Although saturated polycarbosilanes are attractive due to their use as ceramic precursors, recent interests in main chain unsaturated polycarbosilanes have unveiled yet another class of organosilane polymers which is much broader in academic and applied scope. Unsaturated polycarbosilanes are best discussed when divided into two types: those possessing an alternating Si-Si (σ conjugated) bond with an organic π-electron system, and those containing isolated Si atoms alternating with isolated olefins.

Conjugated (alternating σ- and π-delocalization) polycarbosilanes are of considerable interest due to their unique electronic properties. In addition to their potential for applications in all of those mentioned previously for the organopolysilanes, these polymers possess enhanced and quite unique electron delocalization which is not clearly understood.

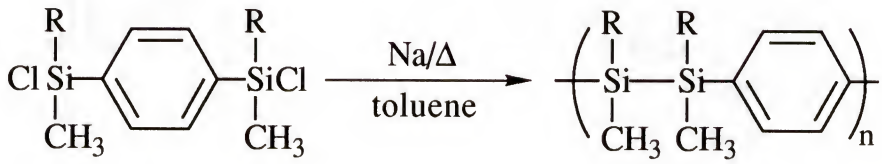


Figure 1.11. Synthesis of poly(disilaphenylene) (R = Et, Ph)

Since the first report of poly(disilaphenylenes) prepared by the previously discussed coupling of chlorosilanes (Figure 1.11) in 1984 by Ishikawa *et al.*,[81] tremendous effort have been devoted to the preparation of an assortment of similar structures. Polymers possessing a regular alternating structure of a Si-Si bond and a π-electron system, such as ethenylene,[82] ethynylene,[83,84] diethynylene,[85,86] furylene,[87,88] and thienylene,[89,90] have been reported. However, the syntheses used to prepare these unsaturated polycarbosilanes are limited to the seldom reproducible and typically low molecular weight forming reactions of dichlorosilanes with sodium or dilithio compounds, or by anionic ring opening polymerization[83] techniques similar to Figure 1.10.2. Ferrocene[91] containing polycarbosilanes, poly(disilaethenes) produced from the modification of existing saturated polycarbodisilanes,[92] and poly[(aryldioxy)silaethenes] formed by the [Pd] catalyzed coupling of cyclosilanes and quinones,[93] all of which possess an isolated Si in the repeat unit, have also been reported.

Perhaps the most elegant synthesis of conjugated disilane polymers is Ishikawa's very recent report of the [Rh] catalyzed polymerization of disiladiynes

(Figure 1.12).[94] Polymers prepared by this route are well defined, semi-conducting when doped, soluble in common organic solvents, and exhibit significant σ-π delocalization through the alternating conjugated system.

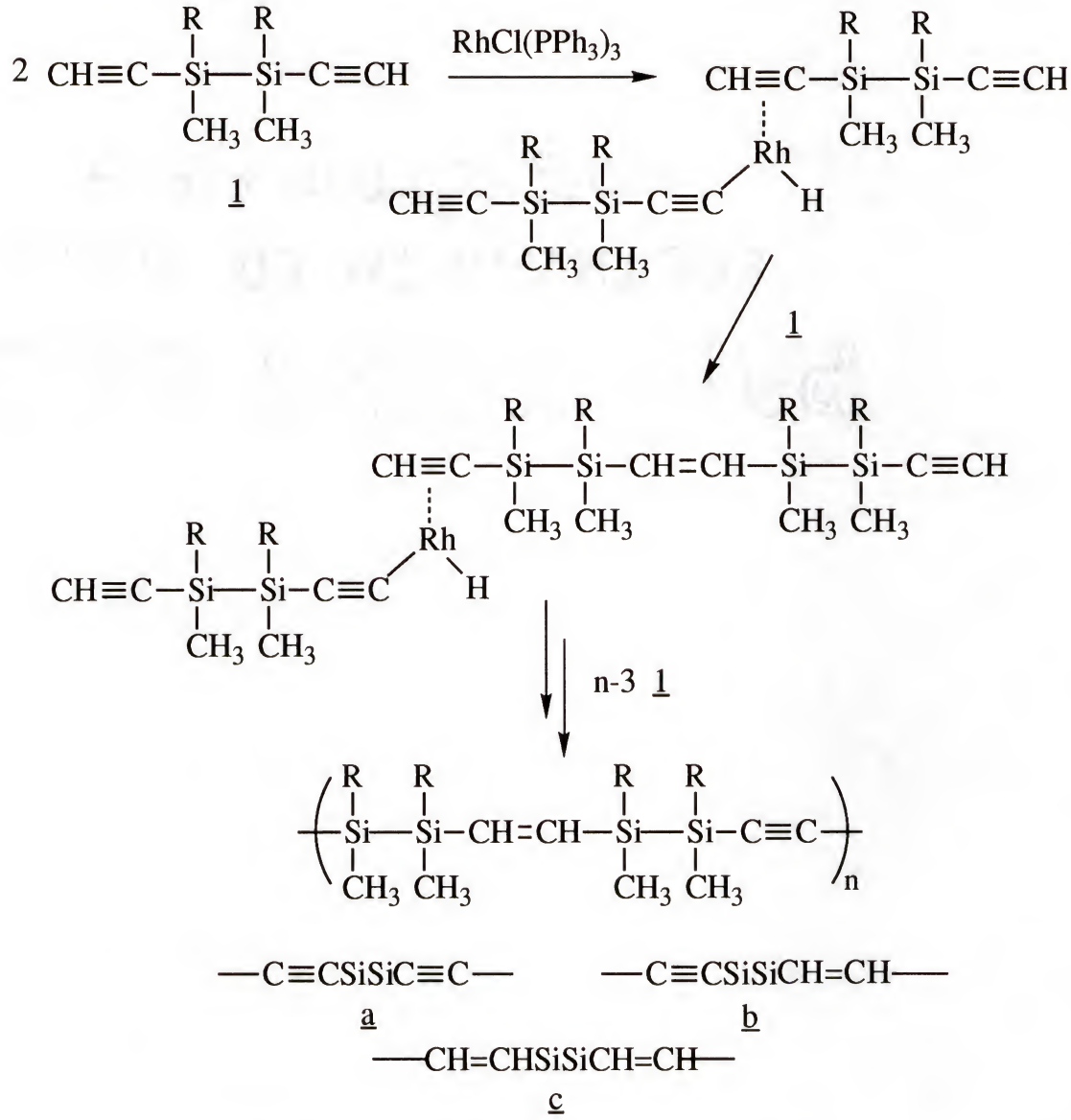


Figure 1.12. Mechanism of [Rh] catalyzed disiladiyne polymerization (R = Ph, Me, Et).

The proposed mechanism of the polymerization begins with activation of an acetylenic C-H bond by the metal center (similar to the role of [Pt] in hydrosilation

reactions), followed by addition across another triple bond producing an alkene as shown in Figure 1.12. Ishikawa *et al.*[94] supports the mechanism by demonstrating that the polymer microstructure contains all possible repeat units, a-c (Figure 1.12) in the predicted statistical ratio of 1:2:1, respectively, since C-H activation should occur in the monomer or polymer with equal probability.[94]

The other type of unsaturated polycarbosilane, those that possess isolated Si atoms alternating with isolated olefins, is much less common primarily due to synthetic limitations. The ease with which nucleophiles are generated from acetylenes and other stabilized unsaturated systems, coupled with the reactivity of halosilanes, provides many straightforward techniques for the previous type of unsaturated polycarbosilane which are not available for polycarbosilanes containing isolated sites of unsaturation. One interesting example which is not easily classified in the manner described here arrives from the transition metal catalyzed cyclopolymerization of dipropargylsilanes (Figure 1.13).[95]

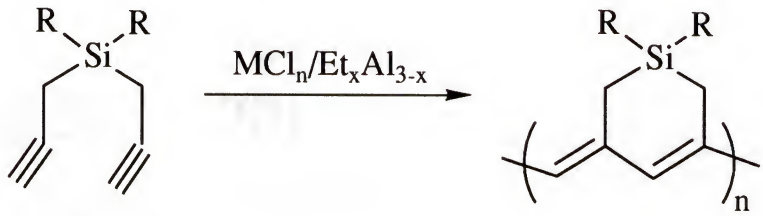


Figure 1.13. Cyclopolymerization of dipropargylsilanes (R = Me, Ph; M = W for n=6, Mo for n=5, and Ti for n=4).

The transition metal catalyzed polymerization of acetylenes to polyacetylenes is well known;[96] yet here, the established concepts of cyclopolymerization, developed by Butler,[8] are employed to include a silicon heterocycle within the repeat unit. This technique is quite general, and in fact, an assortment of dipropargyl monomers containing various functionalities have been prepared.[97]

Titanium based catalyst systems, such as that depicted in Figure 1.13, are general for the Ziegler-Natta[98,99] type chain addition polymerization of olefins; however, the Mo and the W based systems are unique in that they are also catalysts for the ring opening metathesis polymerization (ROMP)[100,101] of cyclic olefins which will be discussed in detail later. The only example of these catalysts being used to prepare unsaturated polycarbosilanes via ROMP is the polymerization of (dimethyl)silacyclopentene (Figure 1.14).[102] This method produced only oligomers of the allylsilane polymer shown in Figure 1.14. More recently, Re based heterogeneous catalysts have been shown to oligomerize (in low yield) diallylsilanes in a condensation manner.[103]

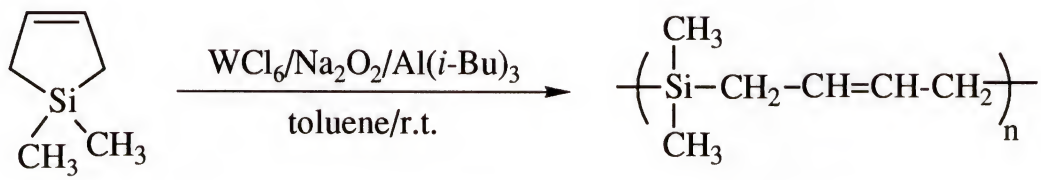


Figure 1.14. Ring opening metathesis polymerization (ROMP) of cyclosilapentene.

By far the largest contribution to polycarbosilanes containing isolated unsaturation has come from the stimulating work of Weber and co-workers over the last four years.[104-112] These researchers have demonstrated that various substituted silacyclopentenes undergo controlled anionic ring opening polymerization initiated by alkyllithium reagents in polar solvents, as shown in Figure 1.15. With this method, unsaturated polycarbosilanes were prepared in high molecular weight (MW ~ 10^5) and typically exhibit good thermal stability with some polymers giving high ceramic yields depending on substituent.[108]

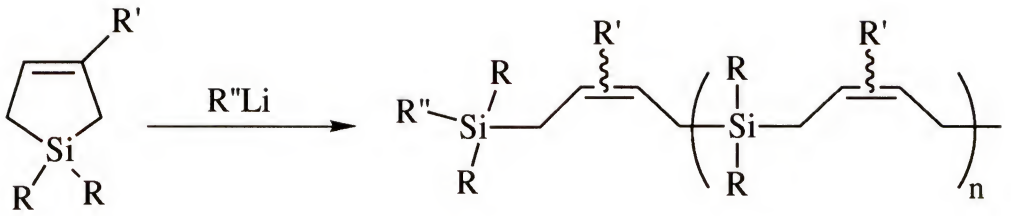


Figure 1.15. Anionic ring opening polymerization of silacyclopentenes (R = Me, Ph, H, vinyl; R' = H, Me; R" = Me, Bu).

The mechanism of the polymerization consists of anionic attack at silicon followed by ring opening and fast attack of the allylic anion intermediate to monomer. No evidence of allylic rearrangement of the intermediate anion is observed, and the stereochemistry at the double bond in these polymers is reported to be completely *cis* in most cases. Copolymers[111] of different silacyclopentenes, benzosubstituted polymers,[105] silaspiro systems,[108] and modification of the polymers by dichlorocyclopropanation[112] have been studied.

It is important to note that throughout this section the developments in polymer chemistry which are pertinent to this dissertation are exhaustive in scope. There have been no examples of direct routes to unsaturated polycarbosiloxanes and only limited examples of unsaturated polycarbosilanes containing isolated silicon and olefin groups.

Transition Metal Catalyzed Olefin Polymerization

This section introduces the background and historical significance of olefin coordination polymerization via transition metal catalysis. Olefin metathesis polymerization, as a specific class of this group, possesses many similarities with the traditional development of transition metal catalyzed olefin polymerization and

is introduced in the next section. These similarities, presented here, are instructive to an understanding and appreciation of olefin metathesis in general.

Throughout the modern development of polymer chemistry, chemists have attempted the polymerization of α-olefins (1-alkyl olefins, e.g., propylene). Although radical, cationic, and anionic initiators polymerize olefins containing polar groups, the energetics of these processes exclude polymerization of α-olefins.[113] More importantly, the stereospecific polymerization of α-olefins, where the pseudochirality of the substituted carbon is regular, has long been desired due to the large differences in properties dictated by the stereospecifity, or tacticity, of the polymer backbone. For example, atactic polypropylene (random pseudochiral centers) is essentially useless, whereas isotactic polypropylene is a strong, high melting, crystalline polymer which finds large-scale use as plastics and fibers.[114]

The field of stereoregular polymer chemistry is traditionally thought to have been born in 1954 when Ziegler and Natta reported new stereospecific olefin polymerization initiators.[115-117] However, after 30 years of confusion and legal battles, finally ending in 1982, R. L. Banks and J. P. Hogan[118] of the Phillips Petroleum Co. were justly recognized as the first to synthesize polypropylene and polyethylene via organotransition metal catalysts in 1951. A number of other researchers, including Zeigler and Natta filed for patents during the same year which described similar catalyst systems. Zeigler noticed unexpected results when aluminum alkyls, then being studied for their use as ethylene polymerization catalysts, were contaminated with nickel salts. Detailed investigations of other transition metal effects followed, leading to the formulation of titanium halide-alkyl aluminum catalyst systems which yielded high molecular weight polyethylene under uncommonly mild conditions. Subsequently, Natta developed

the synthesis and accurate characterization of psuedochiral polypropylene and was, reportedly, the first to detail the revelation of stereoregular polymers.[119]

The initial discovery by Banks and Hogan and the work of Zeigler and Natta has had tremendous impact on the world and is truly one of chemistry's most significant highlights for which Ziegler and Natta both received the 1963 Nobel Prize in chemistry.[119] Banks and Hogan, despite the early unfortunate misrecognition, finally received credit as the discoverers of polypropylene in 1987, as they were awarded the Perkin Medal for outstanding contributions to applied chemistry.[118] Banks later went on to play a key role in the discovery and development of the olefin metathesis reaction, as described in the next section.

The mechanism by which stereospecific polymerization occurs is not entirely understood and varies with the catalyst system. The most thoroughly studied catalyst system has been $TiCl_3/AlEt_3$. The generally agreed mechanism can be expressed in two similar types; a bimetallic mechanism where the propagating species contains both metals, or a monometallic mechanism where only the titanium metal center is used.[98,99] Both mechanisms contain similar steps yet the transition states vary, and for the purposes of this introduction, only the monometallic mechanism, first proposed by Cossee,[120] is discussed (Figure 1.16).

The mechanism begins with π-coordination of the monomer into a vacant orbital at the metal center in a stereospecific manner dictated by the transition metal complex. A metallacyclobutane transition state can then be written to better visualize bond movement. Monomer then inserts into the polymer chain creating a new vacant orbital. If propagation continues via monomer complexation with this species then syndiotactic (alternating pseudochirality) would result, whereas isotactic propagation requires a migration step which creates the original vacant site. The mechanism in Figure 1.16 outlines the general understanding of coordination addition polymerization, which remains in debate today,[99] and

represents one of the two extreme pathways from which polymerization occurs based on subtle differences in catalyst and monomer.

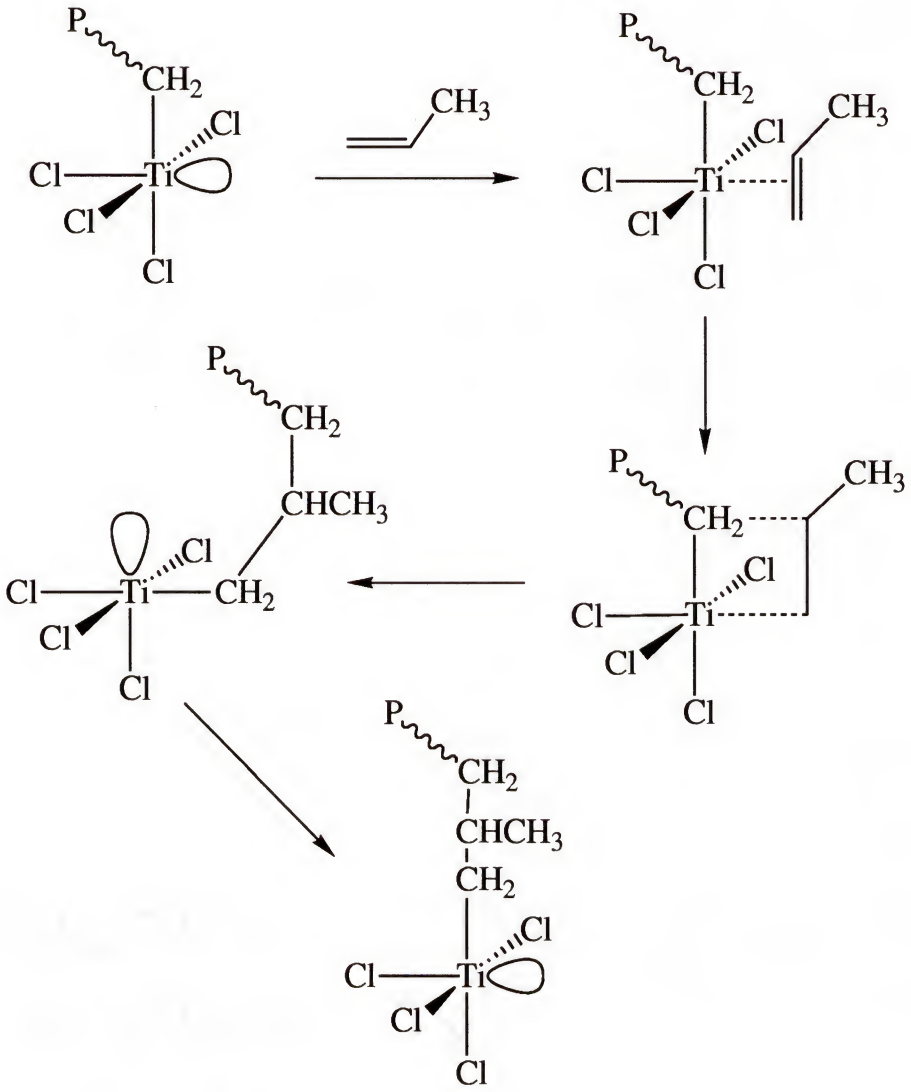


Figure 1.16. Monometallic mechanism for isotactic polymerization of propylene (P = polymer).

Since the initial reports of these new initiators, or Ziegler-Natta catalysts, many derivations have been constructed and refined for very specialized applications.[99] In general, Ziegler-Natta catalyst systems consist of an organometallic compound or hydride of a Group I-III metal (e.g., $AlEt_3$, $AlEt_2Cl$,

$ZnEt_2$) with a Group IV-VIII transition metal (typically halide) component (e.g., $TiCl_3$, VCl_4, $CpTiCl_2$, $Cr(acac)_3$).

In due respect for the decades of efforts devoted to α-olefin polymerization, it must be mentioned that the current "state-of-the-art" Ziegler/Natta-type olefin polymerization catalysis is probably best exhibited by the work of Ewen and co-workers.[121-123] These researchers, at the Fina Oil and Chemical Co., developed extraordinarily useful homogeneous catalysts based on Group IV metallocenes. It was found that chiral Hf and Zr metallocenes induce complete stereochemical control over the polymerization of propylene, and offer tactic-specific polymers of a degree never before possible, and to date unsurpassed.[122]

The tremendous advances in Ziegler/Natta polymerization which have been made, in scope of both catalyst and monomer type, founded the development of a new polymerization catalysis based on the ring opening of cyclic olefins. Cycloalkenes undergo Ziegler/Natta polymerization across the double bond, yet ring opening metathesis polymerization (detailed in subsequent sections) can also occur under appropriate conditions yielding a polyalkenylene with a particular geometric stereochemistry (Figure 1.17). Natta[124] was probably the first to observe this unprecedented result when studying the polymerization of cyclopentene.

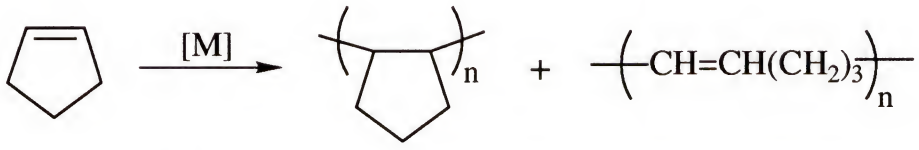


Figure 1.17. Mixed Ziegler-Natta and ring opening metathesis polymerization of cyclopentene.

In general, chromium, vanadium, and titanium based initiators yield mixtures of the ring opened and addition polymer (typically in excess) with cycloalkenes,

whereas molybdenum and tungsten based catalysts yield predominantly the ring opened unsaturated polymer.[99,125] Hein[126] demonstrated that some catalysts systems like, WCl_6/Bu_4Sn will specifically homopolymerize cyclopentene via ring opening metathesis polymerization, while also initiating ethylene polymerization via Ziegler/Natta chemistry within the same solution.

Such is the subtle interface between Ziegler-Natta polymerization and olefin metathesis. Perhaps the clearest example transcends from the fact that most of these catalyst systems polymerize acetylenes to polyacetylenes which is the expected result by either Ziegler-Natta or metathesis mechanisms.[96,100] Many researchers have strived for an understanding between the mysterious interface of these two brothers[127,128] and have, for the most part, achieved limited success. Nevertheless, the ability of these organometallic compounds to adhere so stringently to olefin addition pathways yet mysteriously drift into ring opening propagation when the monomer is cyclic has captured a great deal of the attention from Ziegler-Natta chemists, still to whom most of the development of olefin metathesis is forever owed.

Historical Development of Olefin Metathesis and Traditional Catalyst Systems

The word "metathesis" originates from the Greek, "meta" meaning change and "tithemi" meaning place. Metathesis in chemistry refers to the interchange of atoms by the movement of bonding electrons to form new bonds. "Olefin metathesis," first coined by Calderon[129] in 1967, is now commonly used to express the interchange of two olefins resulting in the formation of two new olefins (Figure 1.18.1). Unlike many organic reactions, olefin metathesis was born in the chemical industry, the development of which has been chronicled in an

excellent review by Streck.[200] The reaction has found remarkable application in a number of important commercial and academic areas, such as fine chemical production (e.g., α-olefins) and pheromone synthesis, yet continues to be most effectively exploited within synthetic polymer chemistry.[130,131]

Olefin metathesis is classified into the following three broad categories: exchange reactions, of which there exists productive and degenerate metathesis (Figure 1.18), polymerization reactions, of both condensation and ring opening types (Figure 1.19), and degradation reactions (Figure 1.20).[100] This section reviews traditional catalyst systems developed for olefin metathesis and offers a brief history of the reaction's discovery, and mechanism elucidation. With the exception of pertinent historical significance, metathesis polymer chemistry will be introduced later.

1.18.1)

1.18.2)

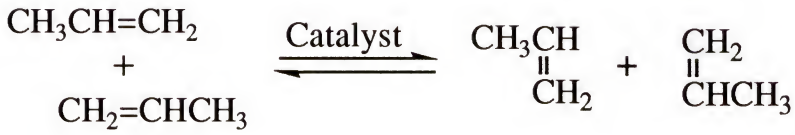
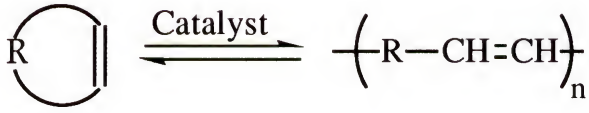


Figure 1.18. Productive (1.18.1) and degenerate (1.18.2) metathesis exchange reactions.

1.19.1)



1.19.2)

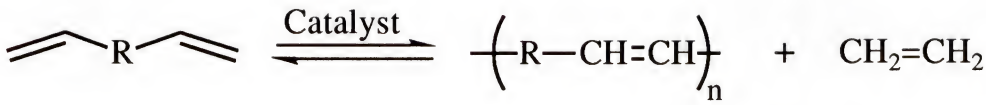


Figure 1.19. Ring opening (1.19.1) and condensation (1.19.1) metathesis polymerization reactions.

Figure 1.20. Metathesis degradation.

The reaction requires an olefin and a metathesis catalyst, both of which are broad in scope and have been extensively reviewed.[100,101] Traditional catalyst systems typically consist of heterogeneous, homogeneous, or supported, transition metal based moieties containing various ligands which almost always accompany Lewis acids as cocatalysts similar to those used in Ziegler/Natta polymerizations.[98,99]

During the early years of metathesis catalyst development, the nature of the true catalytic species eluded researchers as they derived empirical relationships based on what little was understood about this new reaction. During and prior to the delineation of the olefin metathesis mechanism--throughout the 1960s and 1970s--a multitude of organotransition metal complexes coupled with different Lewis acids were explored. The most significant catalyst systems were based on Ti, Zr, and Hf of Group IVA; V, Nb, and Ta of Group VA; Cr, Mo, and W of Group VIA; Re of Group VIIA; and Ru, Rh, Os, and Ir of Group VIIIA. These metals, commonly employed as halides or oxohalides, accompanied Lewis acid components of which the most common were alkyls and organohalides of Al, Zn, and Sn.[100] Most homogeneous catalyst systems react under mild conditions at or

below room temperature and are somewhat restricted to hydrocarbon alkenes due to unfortunate intolerances toward many functional groups. In particular, homogeneous transition metal complexes of W and Mo are today considered the most active, of which popular examples of the early types include $WCl_6/EtOH/EtAlCl_2$,[132,133] $WCl_6/BuLi$,[134] $WOCl_4/SnMe_4$,[135] and $MoCl_2/(NO)_2L_2/Al_2Me_3$.[136]

The first detailed studies of the olefin metathesis reaction, using Zeigler/Natta type coordination catalysts like, $WCl_6/EtAlCl_2$, were reported by Calderon *et al.*[137] with the Goodyear Tire Co. in 1968. Transition metal halides coupled with Lewis acid cocatalyst of this type were developed early in the history of olefin metathesis and would soon prove to be the most active and by far the most studied catalyst/cocatalyst systems. This work, however, was preceded by patent disclosures as early as 1957[138] reporting the ring opening polymerization of various cycloalkenes on supported oxide catalysts such as MoO_3/Al_2O_3. These early reports quickly alerted chemists as to the commercial value of this reaction. Investigations of olefin metathesis applied to polymer chemistry continued to fuel its development leading to the first publication by Truett *et al.*[139] in 1960 which detailed the polymerization of norbornene (Figure 1.21). Since then, the polymerization of various substituted norbornenes has dominated accounts of ring opening metathesis polymerization (ROMP)[100,140] and is discussed in greater detail in subsequent sections.

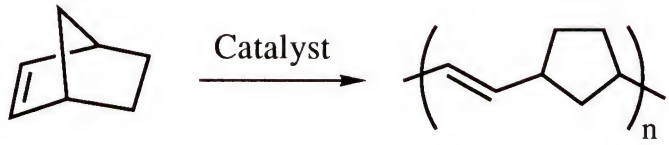


Figure 1.21. The first reported olefin metathesis reaction.

The metathesis of propene (Figure 1.18.1) was first reported in 1964 by Banks and Bailey,[141] of polypropylene fame, and later by Bradshaw *et al.*,[142] where both employed heterogeneous supported oxide catalysts at elevated temperatures. The terms "dismutation" and "disproportionation" were used by Bradshaw *et al.* to describe the process which was proposed to occur through a "quasicyclobutane" intermediate (Figure 1.22),[142] and was the first attempt to explain the mechanism of olefin metathesis. The quest for the true mechanism by which olefin metathesis occurs became a spectacular multidisciplinary mission, of which excellent reviews have detailed.[100,101,122,143]

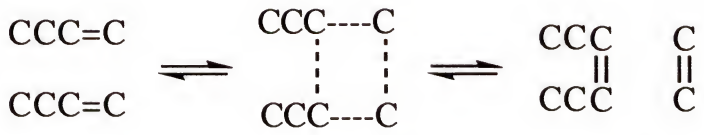


Figure 1.22. Proposed "Quasicyclobutane" mediated metathesis.

Calderon and co-workers, in their classic 1968 paper,[137] offered additional support and detail for this mechanism (Figure 1.23) which vaguely resembles the movement of electrons proposed in Zeigler/Natta mechanisms of the day. It is interesting to note that Cossee's mechanism for the Zeigler/Natta polymerization of propylene (Figure 1.16) was reported in 1964--the same year Bradshaw *et al.* proposed the quasicyclobutane intermediate.[141] Calderon's proposal required bisolefin-metal complex formation followed by "transalkylidenation" where the double bonds could rearrange while centered around the metal, followed by olefin exchange to free a newly formed olefin. This mechanism, which became known as the "pairwise mechanism," was well supported by similar known processes which involved a 4-centered transition state held together by delocalized σ bonds (i.e., Zeigler/Natta-type intermediates) and did in fact explain the product mixtures observed (Figure 1.23).[137]

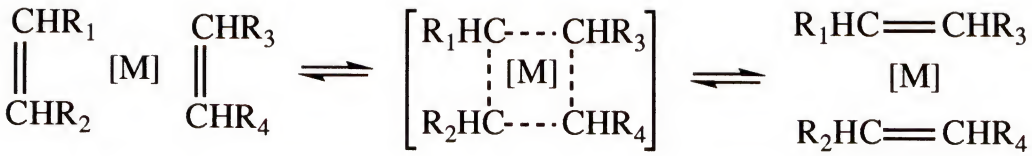


Figure 1.23. Proposed 'pairwise' mechanism for olefin metathesis.

The debate ensued for the next several years while various researchers questioned the structure and energetics of the intermediate quasicyclobutane complex.[101] Herisson and Chauvin[144] began the cascade of evidence which eventually disproved the "pairwise" mechanism when he demonstrated that the cross metathesis reaction, catalyzed by $WOCl_4/Bu_4Sn$ or $WOCl_4/Et_2AlCl$, between an unsymmetrical acyclic olefin and cyclopentene resulted in a statistical mixture of products at essentially zero reaction time (Figure 1.24).

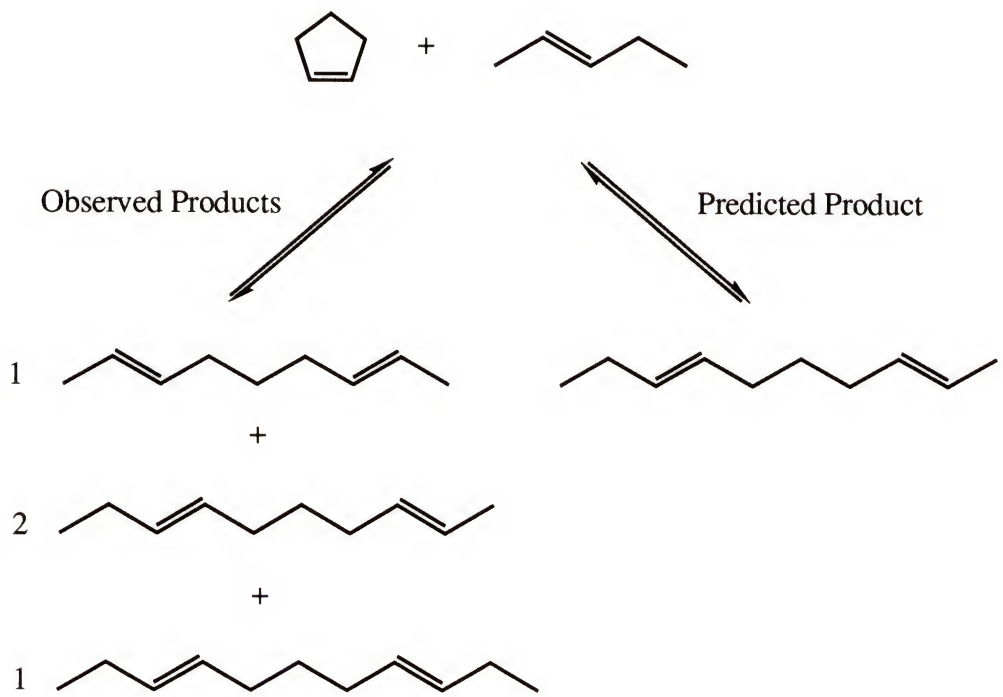


Figure 1.24. Observed statistical ratio vs. predicted products for the pairwise mechanism during cross metathesis.

A pairwise mechanism, for the reaction above, would have predicted only the cross metathesis between cyclic olefin and acyclic olefin at low conversions. This prompted Chauvin to invoke a metal carbene (i.e., a metal carbon double bond) mechanism in order to explain the results (Figure 1.25).

The non-pairwise or metal carbene mechanism requires that a metal carbon double bond be initially generated from the catalyst system or some combination with the olefin. Alkylation of the transition metal by the alkyl aluminum component followed by elimination or in some combination with the olefin is considered to be the general sequence of events.[100] After the carbene is generated, olefin reacts producing a metallacyclobutane adduct intermediate which then productively cleaves to produce the metathesis product (Figure 1.25). A metal carbene, containing an olefin fragment requires only one other olefin to form a new alkene and therefore should not discriminate between reagents and afford a statistical product mixture. The pathway is conceived as an equilibrium process where productive and degenerate cleavage of the metallacycle adduct is determined by a thermodynamic equilibrium.

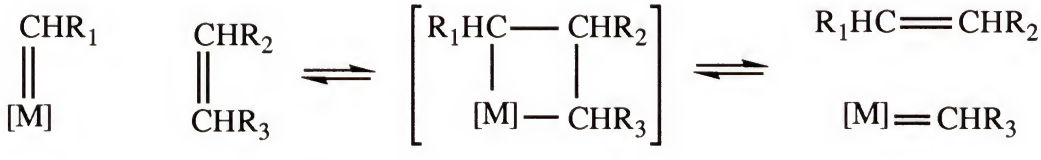


Figure 1.25. Chauvin's metal carbene mechanism.

Although instrumental in demolition, the experiment outlined in Figure 1.24 did not alone disprove the pairwise mechanism. The case where olefin exchange is slower than metathesis could be argued which could account for the statistical distribution of products.[145,146] This "sticky olefin" mechanism is most clearly rationalized on the basis that coordination of the metal to the metathesis product formed last and a new olefin would be most likely in a pairwise catalytic cycle.

The "sticky olefin" mechanism could also explain why high molecular weight polymer was obtained from the polymerization of strained cyclic olefins even at low conversions, indicative of a chain process.[147] A pairwise mechanism predicts polymerization of cyclic alkenes to give only macrocyclics in a stepwise, monomer combination fashion. Polymer chemists of the day continued to share in the destruction of the pairwise mechanism and detailed studies by Scott *et al.*[148] demonstrated that polyalkenes produced by ring opening metathesis polymerization of strained rings were in fact linear. Furthermore, the low molecular weight cyclic olefins that were present form only via an intramolecular metathesis or "back biting" pathway, a reaction unplausible for the pairwise scheme yet solely predicted for the metal carbene mechanism.[149]

Ideal support for the new carbene mechanism envisioned an isolable metal carbene which would undergo metathesis, yet the only known metal carbenes of the day were highly functionalized Fischer-type carbenes[150] and were unreactive toward olefins. Not until four years after Chauvin's proposal did metal carbenes show metathesis activity. Casey and Burkhart,[151] in 1974, prepared a hexacoordinate tungsten carbene which underwent productive olefin metathesis exchange (Figure 1.26) and also facilitated the ring opening polymerization of cyclooctadiene.

Figure 1.26. First metathesis active metal carbene.

This finding offered tremendous support for Chauvin's carbene mechanism, yet ultimately, the pairwise mechanism was defeated under experimental assault by Katz and McGinnis.[152] Through careful control of kinetics containing

thorough definitions of zero reaction time, Katz made use of Chauvin's ideas and revisited the cross metathesis between cyclic and acyclic olefins, yet this time using two symmetrical acyclic olefins (Figure 1.27). The products at time zero predicted for the pairwise mechanism requires that $C_{14}/C_{12} = 0$, however this ratio was precisely observed to be greater than 1.

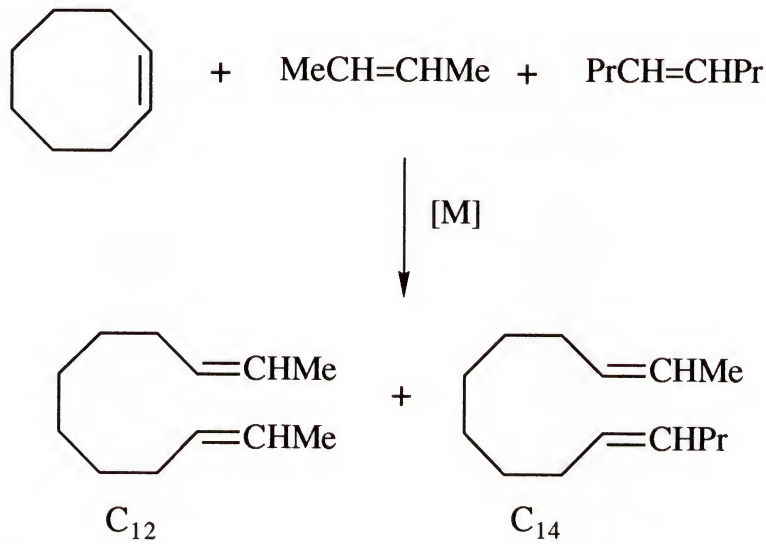


Figure 1.27. Katz's cross metathesis experiment.

Subsequent studies by Katz and Rothchild,[153] applied to 2,2'-divinylbiphenyl and its cross metathesis with the deutero analog gave a mixture of isotopes explainable also, only by a non-pairwise metal carbene mechanism.

With the metal carbene mechanism firmly placed within a thriving community of active explorers, efforts to prepare isolable and retrievable metal carbene catalysts flooded the scene.[100,101,130] Tebbe *et al.*[154] reported the first metal carbene which catalyzed metathesis and could be isolated at the end of the reaction. Howard, Lee, and Grubbs[155] later demonstrated that Tebbe's titanocene chloride alumiunum alkyl complex formed isolable metallacyclobutane adducts which themselves catalyzed metathesis, thereby confirming the proposed

intermediate in the Chauvin metal carbene mechanism (Figure 1.25). These adducts provided the first Lewis acid free ROMP catalysts.

During this time Schrock and co-workers[156,178] began reporting the preparation of stable and isolable Ta, Nb, and W carbenes (or alkylidenes) which proved to be good metathesis catalysts. Schrock's work would later become key to the development of highly active metathesis catalysts and eventually lead to the synthesis of well defined Lewis acid free metal alkylidenes and, seemingly ultimate control over olefin metathesis reactions.[157]

Olefin Metathesis of Silicon Functional Molecules

The olefin metathesis reaction is well known among organic synthetisists, and has appeared in many examples involving the syntheses of specialty molecules.[131] However, the practical utility and scope of olefin metathesis has been somewhat limited due to the functionality sensitive catalyst systems to which the reaction is traditionally confined. Many systems resemble the polarized ylide type complexes which undergo Wittig chemistry with carbonyls and are intolerant to acidic protons as well.[158] Nevertheless in some special cases many functionalities such as -COOR, -OCOR, and -OR have been shown compatible with classical cataysts systems.[100,101,158] Well defined contemporary catalysts have overcome these limitations and will be introduced in the next section.

Alkenylsilanes encompass an essential class of reagents which find wide use in organic synthesis.[15,159,160] However, their applications in polymer chemistry, as described earlier, have been limited to but a few somewhat unreliable techniques. As mentioned in a previous section, the only silicon containing polymer prepared by olefin metathesis prior to the work detailed in subsequent chapters of this dissertation was poly(1,1-dimethyl-1-silapent-3-ene) (Figure 1.14).

Oligomers are obtained from the ring opening polymerization of silacyclopentene[102] or from the condensation of diallyldimethyl silane.[103] Metathesis condensation of diallylsilanes, using Re_2O_7/Al_2O_3 or Re_2O_7/Al_2O_3-$Sn(C_4H_9)_4$ gives predominantly five and six[161] memembered cyclic olefins in addition to low yields of linear oligomers (Figure 1.28). Allyloxysilanes,[162] as well as buteneylsilanes,[163] have also been shown to undergo metathesis when catalyzed by WCl_6 based systems.

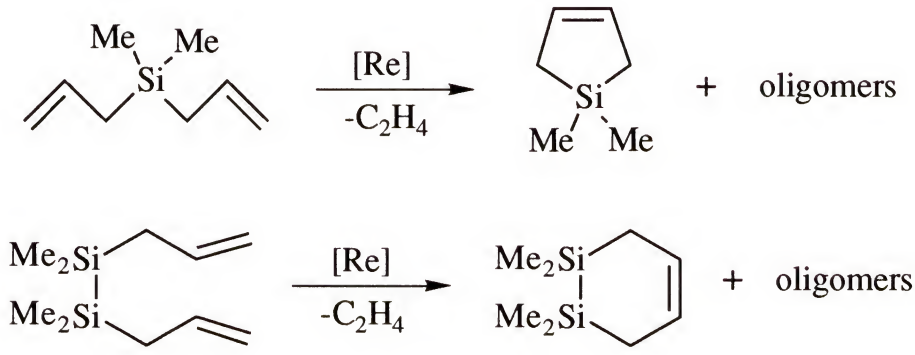


Figure 1.28. Cyclization of diallyl silanes using Re-based catalyst.

The metathesis of vinyl silanes has been of some interest due to their unique reactivity and important applications in organic synthesis such as the stereoselective synthesis of substituted alkenes.[15] Vinylsilanes were probably first used in metathesis reactions by Dolgoplosk *et al.*[164] as degradative chain transfer agents during ring opening polymerizations. The carbene generated from the reaction of $CH_2{=}CHSiMe_3$ with an active polymer using the classic $WCl_6(OR)_2/EtAlCl_2$ catalyst system gave the inactive carbene, $[W]{=}CHSiMe_3$, and vinyl terminated polymer. It was later shown, however, that vinylsilanes do undergo self-metathesis when catalyzed by MoO_3/Al_2O_3 or the Re based catalyst systems mentioned above for allyl silanes to give bis(silyl)ethenes.[165,166] In addition, alkenylsilanes have also been reported to undergo cross metathesis with simple alkenes[163,167] and polyalkenes.[168,169]

Since these initial reports on the metathesis of silicon containing olefins, Marciniec and coworkers[170-174] have initiated a comprehensive investigation concerning the metathesis of alkyl and alkoxyvinylsilanes using various Ru and Rh based catalyst systems. In a classical example of serendipity, these researchers discovered, while studying the hydrosilative activity of various and simple Ru(II) and Ru(III) complexes, e.g. $RuCl_2(PPh_3)_3$, that catalytic metathesis of alkoxyvinylsilanes was a competing reaction (Figure 1.29).[170]

$$2\ (RO)_nMe_{3-n}SiCH{=}CH_2 \xrightarrow[-C_2H_4]{[Ru]} (RO)_nMe_{3-n}SiCH{=}CHSiMe_{3-n}(OR)_n$$

Figure 1.29. [Ru] catalyzed metathesis condensation of alkoxyvinylsilanes.

In addition to bis(silyl)ethanes, when reacting alkoxysilanes ($(RO)_nMe_{3-n}SiH$) with alkoxyvinylsilanes, bis(silyl)ethenes and ethylene were also produced. Self-metathesis occurs with or without the presence of the alkoxysilane when treated with various catalysts like, $RuCl_2(PPh_3)$ or $RhCl(PPh_3)$. Marciniec's work constitutes an unique example of highly active metathesis catalysis with a classical type transition metal complex without the presence of a Lewis acid cocatalyst.

Initially Marciniec *et al.*[171] proposed a mechanism involving a hydride complex which rearranges to give an active metal carbene. However, very recent studies by these researchers[174] indicate that a carbene is not generated and that the catalysis is composed of a variety of σ-complexes as depicted in Figure 1.30.

Complexation of the olefin to the electrophilic metal center is followed by [Ru] insertion into the C-H bond and vinylsilane addition to the metal. Ethylene elimination then gives a [Ru]-Si bond wherein another molecule of vinylsilane inserts followed by reductive elimination of the homometathesis product while regenerating the olefin complex.[174] Detailed efforts by Marcinec and co-workers

are currently providing concrete development of this unique application of metathesis chemistry.[171-174]

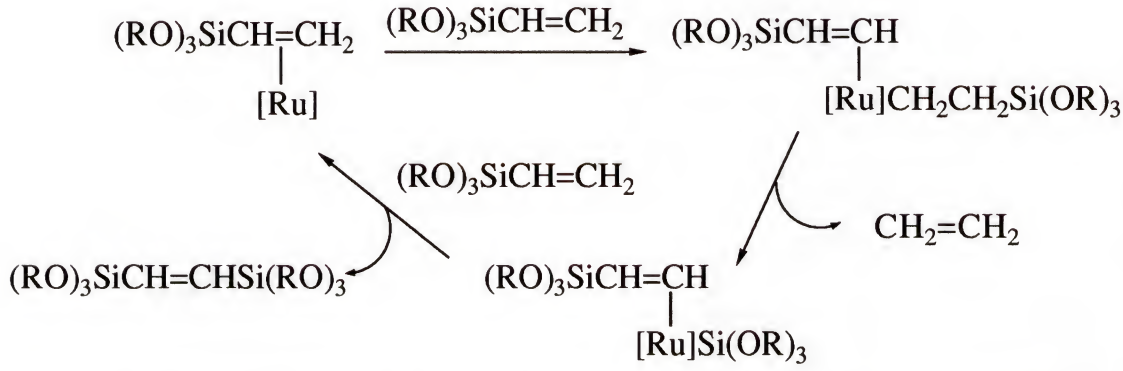


Figure 1.30. Proposed mechanism for the metathesis of vinylalkoxysilanes.

Attempts at polymer synthesis via condensation metathesis of divinylsilanes and bisvinylsiloxanes have been briefly mentioned,[171] yet the moderate conversions reported for these catalysts are not suitable for the high conversions required for step growth polymer chemistry. The specific requirements of step polymer chemistry will be discussed in later sections of this chapter.

Development of Lewis Acid Free Alkylidene Catalysts

Although stabilized Fischer-type carbenes (those containing a stabilizing heteroatom on the carbene carbon) were prevalent during the development of the olefin metathesis mechanism, these complexes initiated metathesis only stochiometrically.[150] The first known carbenes which exhibited metathesis catalysis; those of Casey[151] (Figure 1.26), Tebbe *et al.*,[154] and Grubbs *et al.*,[155] required the presence of Lewis acid cocatalysts. Grubbs and Tumas,[155,175] used Tebbe's titanocene alkylaluminum chloride complex to prepare various substituted and isolable titanacyclobutanes which catalyzed metathesis via an unisolable

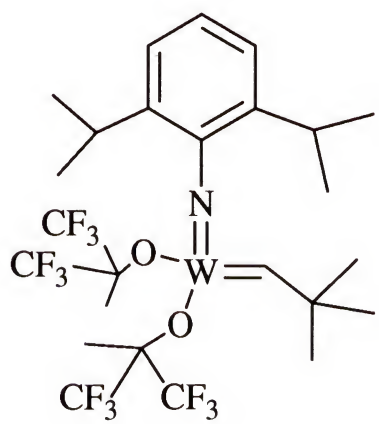
titanacarbene. However, in 1973, Schrock (then with the duPont research group and later with MIT) began an exhaustive study in search of well defined Lewis acid free metal carbene (or alkylidene) catalysts which was ultimately achieved in 1986.[157]

Early work with classical catalysts systems[100] like $WCl_6/EtAlCl_2$ and the successful modeling of olefin metathesis intermediates suggested that the best catalytic metal alkylidenes existed in the highest possible oxidation state and possessed low coordination numbers.[176] Since these realizations, many stable and isolable transition metal alkylidenes have been prepared, the most studied being those containing highly active d^0 configurations of Ti, Zr, Ta, W, Mo, and Re.[177] The first isolable d^0 alkylidene complex, Ta(CH-t-Bu)(CH-t-Bu)$_3$, was prepared by Schrock in 1974, yet this complex did not catalyze productive metathesis.[178] Schrock later prepared the first stable and well characterized transition metal alkylidenes of the type, M(CH-t-Bu)(O-t-Bu)$_2$(PMe$_3$)Cl (M = Nb, Ta) which did catalyze the metathesis of 2-pentene.[179] However, W(VI) alkylidenes soon followed with the synthesis of W(O)(CH-t-Bu)(PMe$_3$)$_2$Cl$_2$, which showed better metathesis activity yet only in the presence of $AlCl_3$.[180] Catalytic activity was also relatively short lived due primarily to reduction of the metal to form olefin complexes.

The chemistry developed by Schrock during the preparation of active transition metal alkylidenes also led to an important area involving the synthesis of alkylidynes.[157] These compounds, such as M(C-tBu)(OR)$_3$ (M = W, Mo), became versatile polymerization catalysts for a variety of substituted and unsubstituted acetylenes and are of significance to the ultimate development of Lewis acid free alkylidene metathesis catalysts.[181,182] Protonation of the alkylidynes gave alkylidenes of the type, W(CH-t-Bu)(OR)$_2$X$_2$, which catalyzed metathesis yet again, only in the presence of $AlCl_3$.[183] The study of these

compounds, however, was a major step in delineating the requirements for Lewis acid free alkylidenes and were similar to alkylidenes prepared earlier by Osborn *et al.*[184]

With the success of high oxidation state, four coordinate tungstalkylidyne complexes, Schrock and co-workers envisioned neutral, four coordinate stable tungstalkylidenes. It was reasoned that a four coordinate W(VI) complex could only be achieved by using an oxo or imido ligand, of which the oxo was discarded since it could not provide any stabilizing steric bulk to the complex. An aromatic imido ligand, such as N-2,6-C_6H_3-*i*-Pr_2, would provide the necessary bulk that prevented deactivation of the catalyst through intermolecular reactions (i.e., dimerization).[185] The first imidoalkylidene complex of this type was reported in 1986 by deprotonation/protonation (with NEt_3) of the amidoalkylidyne, W(C-t-Bu)(NHR)(dme)Cl_2, to give W(CH-t-Bu)(NR)(dme)Cl_2 which could then be derivatized with various alkoxy substituents of which catalyst 1 in Figure 1.31 was found to be the most active.[186] Catalyst 1 provided the first example of a well-characterized, highly active, neutral Lewis acid free olefin metathesis catalyst and the beginning of a revolution in metathesis chemistry.



1

Figure 1.31. Lewis acid free Schrock alkylidene.

Olefin metathesis catalysts of this type (1, as well as the earlier developed transition metal alkylidenes[178]) are known as "Schrock alkylidenes" and are altogether unique due to their stability and high reactivity. With the advent of improved syntheses for these well defined catalysts, detailed studies were targeted for better understanding of the olefin metathesis reaction.[187,188] Schrock alkylidenes allowed many substituted and unsubstituted metallacyclobutanes to be characterized, which provided mechanistic data previously unattainable from classical catalysts systems.[177,187-190]

Dramatic effects on Schrock alkylidene activity could be easily altered by varying the electron withdrawing nature of the alkoxide ligand. For example, catalyst 1 (OR = $OCCH_3(CF_3)_2$) metathesizes *cis*-2-pentene at a rate of ~1000 turnovers/min while under the same conditions for OR = O-*t*-Bu, *cis*-2-pentene is metathesized at a rate of only ~2 turnovers/h.[187] Experimental evidence indicates the primary reason for the differences in activity is that the stability of tungstacyclobutanes is greater the more electophilic the metal center is, or the greater the electron withdrawing power of the ligands. Unfluorenated alkoxides form unstable metallacycles slowly whereas perfluorenated alkoxide ligands such as, OR = $O(CF_3)_2CF_2CF_2CF_3$, result in stable and unreactive metallacycles and low metathesis conversions. A median and perhaps optimal electronic effect is observed when OR = $OCCH_3(CF_3)_2$ as in catalyst 1.[177,185] A simpler explanation is that initial coordination or nucleophilic attack of the olefin to the metal is rate determining and therefore is dictated by the electrophilicity of the metal, whereas an overly electrophilic metal results in slow metallacycle formation.[185] The reactivity of Schrock alkylidenes is also governed by the size of the alkylidene ligand. Studies have indicated that the neopentylidene catalyst (1

in Figure 1.31) can be ~100 times less reactive than the propylidene analog yet is much more stable than its less bulky counterpart.[185]

Since the M=CHR bond's reactivity is changed only on steric grounds when substituent size is altered, catalysts based on other transition metals, yet of the same design as 1, were also investigated in attempts to provide a more functionality tolerant metathesis catalyst. Catalyst 1 does promote metathesis among functionalized olefins like methyl oleate but is eventually deactivated due to Wittig-like chemistry which destroys the alkylidene ligand (Figure 1.32).[187] Due to the polarized M=CHR bond, many alkylidenes containing metals such as, Ta, Ti, and Zr can behave like ylides and undergo these undesired paths.[177,191]

Figure 1.32. Wittig-like chemistry of tungstalkylidenes.

However, it was found that the molybdenum analog of catalyst 1, first reported by Murdzek and Schrock in 1987,[192] contains a significantly less polarized M=CHR bond and is much more tolerant to the carbonyl functionality.[193] It should be noted that all of these catalysts are extremely sensitive to nucleophiles (i.e., water), acidic protons (i.e., alcohols), and oxygen. Nevertheless, the molybdenum catalyst does not react with excess ethyl acetate or N,N-dimethylformamide over a period of two weeks indicating that more aggressively functionalized olefins could then be metathesized efficiently.[194]

An elegant example illustrating the utility of the molybdalkylidene to organic synthesis was shown most recently by Grubbs and Fu where various oxygen[198] and nitrogen[199] containing heterocycles could be prepared in excellent yield via the metathesis cyclization of dienes (Figue 1.33).

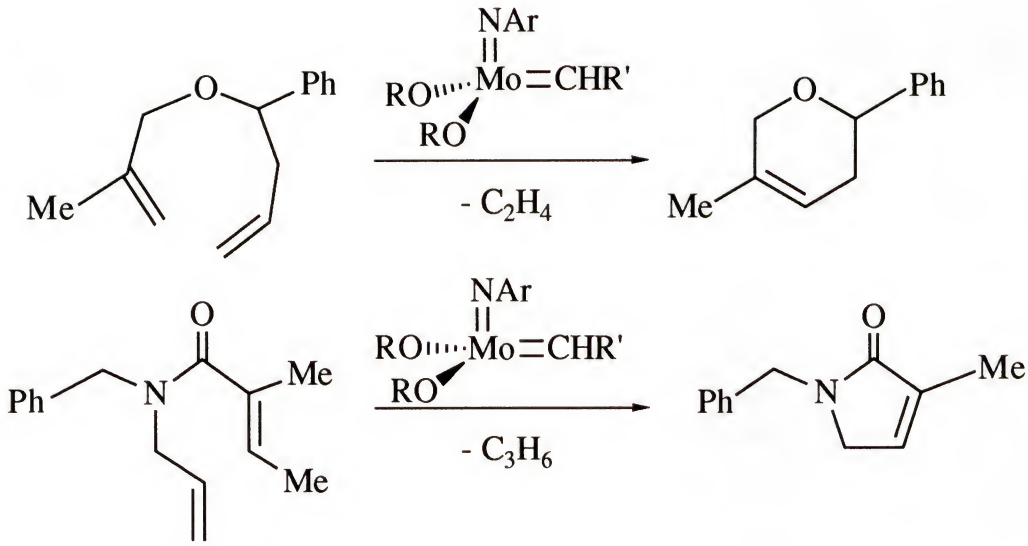


Figure 1.33. Metathesis cyclization of functionalized dienes (Ar = 2,6-C_6H_3-*i*-Pr_2, R = $CMe(CF_3)_3$, and R' = *t*-Bu).

Examples involving the metathesis of functionalized olefins were quickly applied to ring opening polymerization chemistry and is discussed in detail in the next section.[195,196] $Mo(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ does react with more reactive carbonyl compounds, such as benzaldehyde and acetone, to give primarily the expected Wittig-type products. Initial studies[194] also suggest that the molybdenum analog of catalyst 1 metathesizes olefins slower than the tungstalkylidene yet these observations have been disputed and the difference in rates of metathesis between tungsten and molybdenum based catalysts appear to be substrate dependent.[197]

Since the development of Schrock alkylidenes in the last six years, many features of the olefin metathesis reaction have become more salient. Answers have been provided from these well defined catalysts which have greatly promoted the attractiveness of olefin metathesis as an extremely useful reaction. Although some questions remain as to the exact details of the many mechanistic steps involved, the use of these catalysts as efficient tools for the controlled

polymerization of cycloalkenes has been the premier focus of study since their invention.[177,185]

Ring Opening Metathesis Polymerization (ROMP)

As discussed in previous sections, olefin metathesis derived its beginnings from uses in polymer chemistry.[100] The observation that certain Ziegler/Natta type catalysts would initiate both chain addition (across the double bond) and ring opening polymerization in a cycloalkene featured the new reactions potential and was rapidly exploited. The industrial giants in polyolefin catalysis, and others,[200] quickly established research programs designed to capitalize on olefin metathesis as a polymerization method for which it was deservingly referred to as "...industrially one of the most successful of all organic reactions."[200]

Several commercial polymers have been produced by ring opening metathesis polymerization (ROMP) using Lewis acidic classical catalysts. The first was *trans*-poly(norbornene) (Figure 1.19) prepared by the $RuCl_3$ catalyzed polymerization of norbornene and sold as Norsorex™ by Cdf Chimie in 1976.[201] Next came *Trans*-poly(octenamer) known as Vestenamer,™ sold by Hülls Corporation in 1980 and was prepared by the polymerization of cyclooctene.[169] Interestingly, polypentenamer was never made commercial despite considerable effort by rubber giants such as Goodyear, Bayer, and others. Poly(dicyclopentadiene), sold as Metton™ by Hercules (Figure 1.34)[202] perhaps best expresses the industrial viability of ROMP[203] since its production makes use of the wonderfully subtle structure/reactivity relationships that ROMP exhibits and applies commercially.

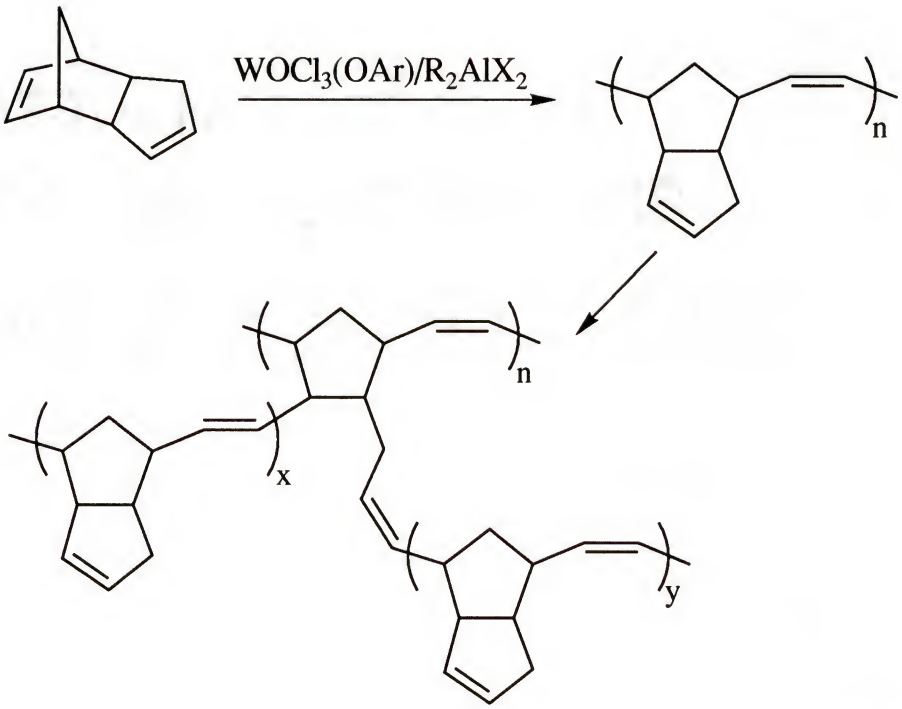


Figure 1.34. Commercial production of Metton™ via ROMP.

Metton™ is prepared by the reaction injection molding (RIM) process where monomer and unactive catalyst components are mixed producing an active ROMP catalyst system. The mixture is then injected into a product mold where linear ring opening metathesis polymerization of the more strained norbornyl olefin occurs first, and cross linking ensues in the mold via ring opening of the cyclopentene group producing a finished thermoset product. No experimental evidence exists as to exactly how cross linking occurs, yet ring opening of the cyclopentene ring is thermodynamically unfavored relative to the ring opening of the norbornene double bond.[204] Secondary cross linking is especially advantageous, whatever the route, since this allows for component homogeneity and convenient injection flow properties before solid product is formed.

The thermodynamic concepts of ring opening polymerizations, in general, are well known and have recently been summarized by Ivin.[205] Polymerization is typically enthalpy driven due to the release in bond angle ring strain in 3 and 4-

membered rings and non-bonded strain for 8, 9, and 10-membered rings resulting from intra-ring atomic interactions. For very large (oligomeric) rings, containing negligible strain, polymerization is entropy driven through the gain of translational entropy in the polymer. The polymerizability of 5, 6, and 7-membered rings is largely dependent on conditions since the magnitude of the enthalpy and entropy terms are very similar.[206] Each cyclic alkene also has associated with it a ceiling temperature, as do all ring opening polymerizations, above which polymerization is not possible due to an overall positive free energy change.[205]

Although these thermodynamic generalizations are easily accepted, kinetic effects dictated by the stability of the propagating alkylidene have been shown to play an important role in the rate of propagation, according to Patton and McCarthy.[206] In a detailed study of the ring opening polymerization of various cyclic olefins possessing differing ring strain, the rates of propagation did not depend on the ring strain, and in fact monomers such as norbornene polymerized at greater rates than monomers possessing much more strain such as cyclobutene. It was rationalized, based on these results and others, that intramolecular coordination of a nearby olefin into the propagating metal alkylidene was more rate determining than actual ring strain (Figure 1.35). A propagating alkylidene containing a ring opened norbornene monomer (a) is not able to coordinate to the metal and compete with an incoming monomer as is the case for cycooctene or cyclobutene monomer (b).

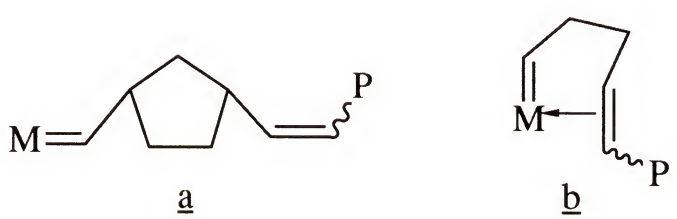


Figure 1.35. Norbornene vs. cyclobutene propagating alkylidenes and proposed coordination effect (P = polymer).

Classical catalyst systems of the type used for commercial applications are sufficient in that precise molecular weight distributions and control of side reactions are seldom an issue. Although the use of these catalysts to polymerize cyclic olefins is vast, Lewis acidic catalyst systems are highly reactive and do not completely discriminate between cycloalkene monomer and olefins within the polymer chain.[100,140] Classical catalyst systems also seldom provide irreversible propagation which subjects the polymerizing system to the thermodynamics of ring-chain equilibrium,[207] and is common for a variety of ring opening polymerizations.[208]

For the most part, ROMP is characteristic of two regimes, 1) a propagating kinetic regime pertaining to early extents of reaction, and 2) a thermodynamic regime where monomer concentration is low and the system is subject to a ring/chain equilibrium.[209-212] Based on extensive studies in this area, some dispute is found concerning whether or not ROMP is actually a chain growth or step growth polymerization.[213] Generally, classical ROMP is considered to fall within the realm of chain growth kinetics, yet as discussed later, classical catalyst systems are, for this discussion, obsolete since well defined Schrock-type alkylidenes give well defined and irreversible polymerizations. Chapter 5 deals with these questions in more detail.

For many years, a goal of polymer chemists has been to synthesize polymers in a highly controlled fashion providing the narrowest molecular weight distributions as possible. This is achieved only if the rate of initiation is faster than (or at least equal to) the rate of irreversible propagation and the rates of termination and chain transfer; i.e., any reaction which interferes with propagation, are negligible relative to propagation. Polymerizations which behave in this manner are referred to as "living" and afford polymers of very narrow molecular

weight distributions (c.a. < 1.1) and predictable degrees of polymerization depending on the ratio of monomer to initiator concentrations.[113] Observance of high polymer at low monomer conversions is indicative of simple chain polymerization (such as radical), whereas a living polymerization exhibits a linear relationship between molecular weight and monomer conversion. Initiation begins at the same time ensuring that propagating chains contain "live" chain ends which consume monomer without interruption. Upon consumption, monomer can be changed during a living system thereby producing block copolymers of well defined structure.[37]

Highly active Lewis acid-free transition metal alkylidenes, described in the previous section, represent a unique class of living polymerization catalysts for the ring opening polymerization of strained cyclic olefins.[175-177,185] The first living ring opening metathesis polymerization was reported in 1984 by Grubbs and Tumas[175] and in 1988 by Novak and Grubbs[214] using titanacyclobutane complexes and norbornene (Figure 1.36).

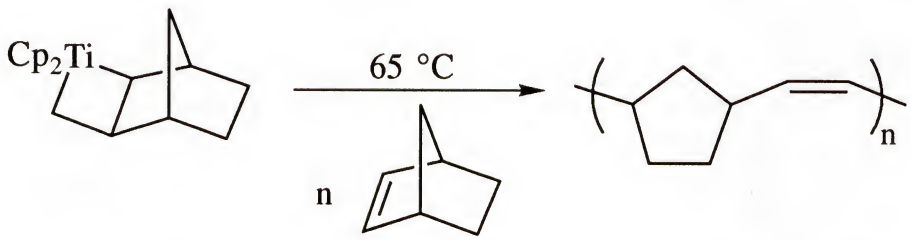


Figure 1.36. First "Living" Ring Opening Metathesis Polymerization.

Since these reports various substituted norbornenes and norbornadienes have been polymerized in a living manner using the aforementioned Schrock-type alkylidenes such as $M(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ for M = W, Mo (see Figure 1.31).[185] These catalysts are ideal for controlled living polymerization since they are relatively unreactive toward the acyclic C=C bonds along the polymer backbone,

yet are extremely reactive towards strained cyclic olefins, even at low temperatures (i.e., -80 °C). Well defined unsaturated polymers produced by this method have led to many specialty applications. In particular, the preparation of polyacetylene and other conducting polymers from polymer precursors or the direct polymerization of cyclooctatetraene have received considerable attention.[97,175,185,215]

While new functionality tolerant ROMP catalysts constitute a great deal of current research, the controlled living ROMP of functional monomers is best accomplished with Schrock alkylidenes of the type, M(CH-t-Bu)(NAr)$(OR)_2$ for M = W, Mo. Notable exceptions include work by Grubbs and coworkers,[216-219] as well as other independent researchers,[220] who very recently demonstrated unprecedented functionality tolerant systems where Ru complexes catalyze ROMP in an aqueous environment. Furthermore, the first air and moisture stable tungstalkylidene catalyst has been prepared by Boncella and coworkers,[221,222] which initiates ROMP in the presence of $AlCl_3$. These works complement efforts devoted to the design of Schrock-like catalysts which are tolerant to some common functionality.

As described in the previous section, the molybdenum based Schrock alkylidene catalyst is more compatible with polar functionality than is the tungstalkylidene. For example, the tungsten catalyst 1, in Figure 1.31, will polymerize *endo,endo*-5,6-dicarbomethoxynorbornene only to low molecular weight oligomers of uncontrolled distribution due to rapid destruction of the alkylidene. Mo(CH-t-Bu)(NAr)(OR) (2), on the other hand, produces high polymer containing a narrow molecular weight distribution from the same monomer in a living manner (Figure 1.37).[193]

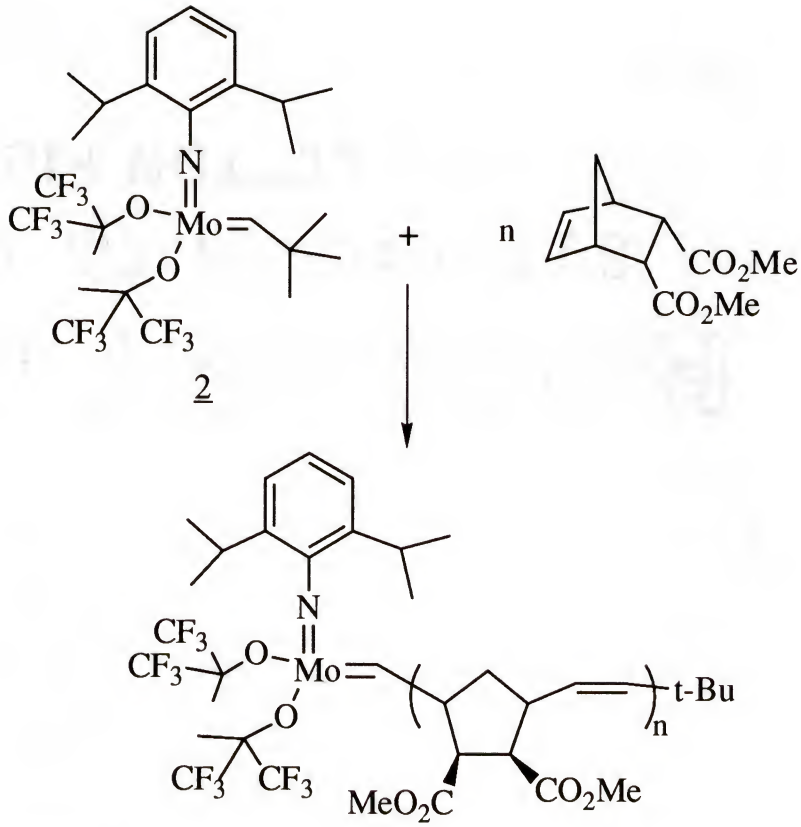


Figure 1.37. Living Polymerization of Ester Norbornenes.

To date, many different functional substituents have been found compatible with molybdalkylidene 2. Substituents containing halogens, imides, ethers, esters, ferrocene, and nitrile have been successfully polymerized to give multi-functional unsaturated polymers.[185,195,223] These well defined functional polymers prepared by controlled ROMP have also provided access to very specialized block copolymers.[184,224-226] Very recently, polymer films containing nanoclusters of silver,[225] gold,[224,225] palladium,[226] and platinum[226] have been constructed from diblock polymers obtained using Schrock's molybdenum alkylidene catalyst. This catalyst has also been shown to be ideal for the controlled synthesis of side chain liquid crystalline polymers.[227]

Acyclic Diene Metathesis (ADMET) Condensation Polymerization

The productive metathesis exchange reaction (Figure 1.18.1) of two acyclic olefins produces two new olefins, yet with no obvious reference to driving force except for the increase in entropy associated with an equilibrium process. However, if the newly formed olefins were removed selectively from the reaction, then the productive metathesis equilibrium would be shifted further and faster to product. Applying the scenario to an acyclic reactant containing two metathesizable olefins (dienes), polymerization should result if high conversions could be achieved. Acyclic diene metathesis (ADMET) condensation polymerization (Figure 1.38) falls under the category of step polymerizations which possess, regardless of the chemistry involved, strict statistical requirements.[113]

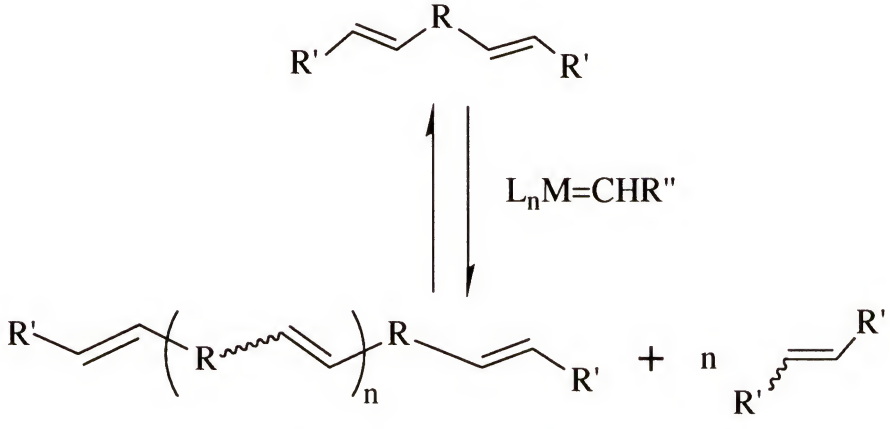


Figure 1.38. Acyclic diene metathesis (ADMET) condensation Polymerization.

Synthetic polymer chemistry is divided into classes by propagation mechanism. In general there are two classes, chain and step propagation polymerizations.[113] The metathesis polymerization of acyclic olefins is defined as an equilibrium step polymerization, condensation type. The term, condensation

type, arises from the liberation of a by-product which advances the reaction. The other possibility for step polymerization is addition type, where the resulting polymer linkage is an adduct of the two monomers, and no atoms are lost (e.g., polyureathanes).

Step polymerizations proceed in a stepwise fashion. Monomer is consumed early in the reaction to form dimers, trimers, tetramers, etc., and the molecular weight is governed by the statistics associated with linking ends of monomer groups. All step polymerizations obey these statistics, oblivious to the nature of the functional groups being connected, and require complete (99.99 %) conversions before high molecular weight polymer is formed. In order to achieve these conversions, the stoichiometry of functional groups must be strictly balanced, and side reactions must be completely obviated. The average degree of polymerization (X_n) is dependent upon conversion and stoichiometry which is governed by the following equation:

$$X_n = 1 + r / (1 + r - 2r\rho)$$

Clearly, the average degree of polymerization, X_n (number of repeat units), depends only on the stoichiometric imbalance ratio, r ($r \leq 1$), and the extent of conversion, ρ (expressed as fractional % functional groups consumed). Considering a step polymerization which contains only one type of functional group, as is the case for metathesis polymerization of acyclic dienes, then stoichiometry is perfectly balanced and the equation reduces to the Carothers equation:[7]

$$X_n = 1 / 1 - \rho$$

A simple plot of the Carothers equation (Figure 1.39) illustrates the fundamental requirement of step polymerizations. Conversions of 99+ % are required if high polymer is to form.

ρ	$\bar{X}_n$
0.8	5
0.9	10
0.95	20
0.99	100
0.995	200

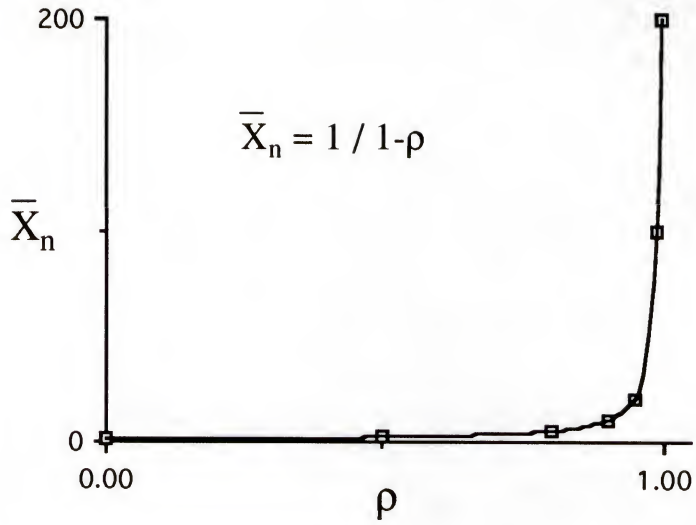


Figure 1.39. Plot of the Carothers equation.

Although attempts to produce unsaturated polymers by the metathesis of acyclic dienes using classical type catalyst systems described earlier has received sparse attention over the last 20 years, the strict requirements of step growth polymer chemistry condemned these early efforts to only limited success.[100,228-230] Dall'Asta *et al.*[228] were the first to report the polycondensation of α,ω-dienes by demonstrating that 1,4-pentadiene and 1,5-hexadiene reacted with traditional Lewis acidic metathesis catalysts to give linear unsaturated oligomers and ethylene. Other early attempts by Doyle[229] and Zuech *et al.*[230] further illustrated the restrictions exhibited by metathesis condensation whereby the use of classical catalyst systems did not result in the formation of high polymer. These Lewis acidic catalysts result in uncontrollable and highly reactive modes of propagation where competing reactions destroy the opportunity for the high conversions required for successful step polymerization.

In 1987, Lindmark-Hamberg and Wagener[231] discovered that the early failures of this reaction were due to competing cationic vinyl addition chemistry and that the elimination of carbocations was absolutely essential before successful

acyclic diene metathesis polymerization could occur. Attempts to polymerize 1,9-decadiene and 1,5-hexadiene to polyoctenamer and polybutadiene, respectively using $WCl_6/EtAlCl_2$ resulted in low conversions of oligomers accompanied by an intractable solid.[231] The solid was rationalized as being a cationically initiated cross linked product of the oligomers. Since most classical catalysts involve a Lewis acid cocatalyst to generate the appropriate carbene, the possibility of vinyl addition chemistry had always been a threat. However, if the desired metathesis reaction is faster than carbocation formation, as is the case for ROMP, then vinyl addition is not favored. The condensation of acyclic dienes is overall (due to competing equillibria to be discussed later) a much slower reaction and therefore is vulnerable to competing vinyl addition chemistry.

Wagener and co-workers carried out two elegant model studies to demonstrate that cross linking via cationic initiation was indeed the reaction which competed with metathesis polycondensation.[231-233] Substituted styrenes were used to test the theory of cation formation since styrene is a well known cationic polymerizable olefin which gives an easily characterized product.[113] When various styrenes were treated with classic Lewis acidic catalyst systems like $WCl_6/EtAlCl_2$, only polystyrene was produced, whereas metathesis products (substituted stilbenes) were not observed (Figure 1.40).[231]

These 1987 results concluded that classical metathesis catalyst systems were not sufficient and that Lewis acid free catalysts were necessary if successful ADMET condensation polymerization was to become a reality. The key to successful ADMET polymerization was demonstrated by Wagener, Boncella, Nel,[232] Duttweiler, and Hillmyer[233] when these researchers employed the Lewis acid free tungstalkylidene metathesis catalyst developed by Schrock *et al.*[186] just one year earlier, $Me_3CCH{=}W(N\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OC(CF_3)_2Me]_2$ (1 in Figure 1.31). Subjecting this new catalyst to the styrene model, the group found that quantitative

metathesis occurs producing only substituted stilbenes completely void of any evidence that cationic addition had occurred (Figure 1.41).[232,233]

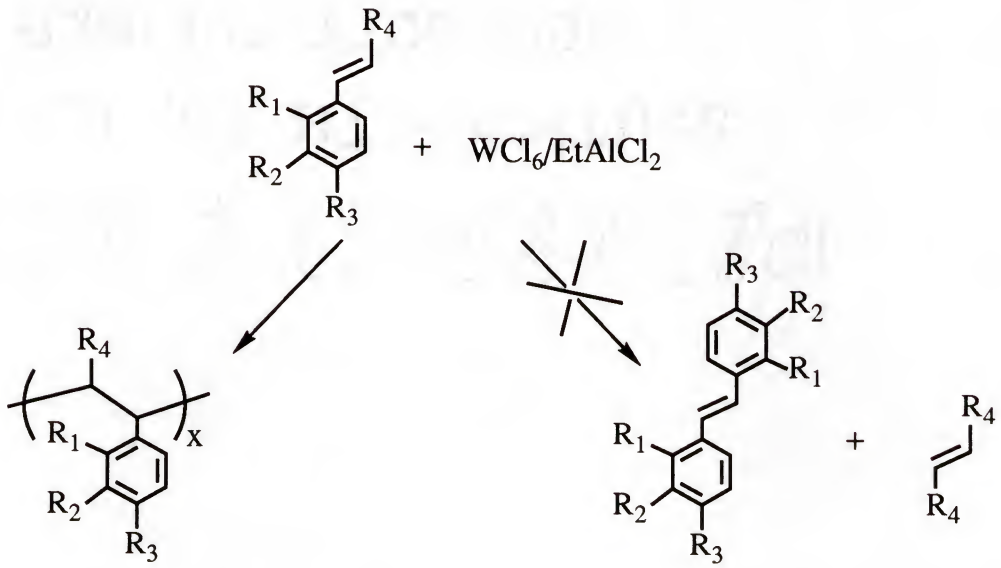


Figure 1.40. Model for cation formation with classical Lewis acidic catalyst systems (substitutions represent various halogens or Me).

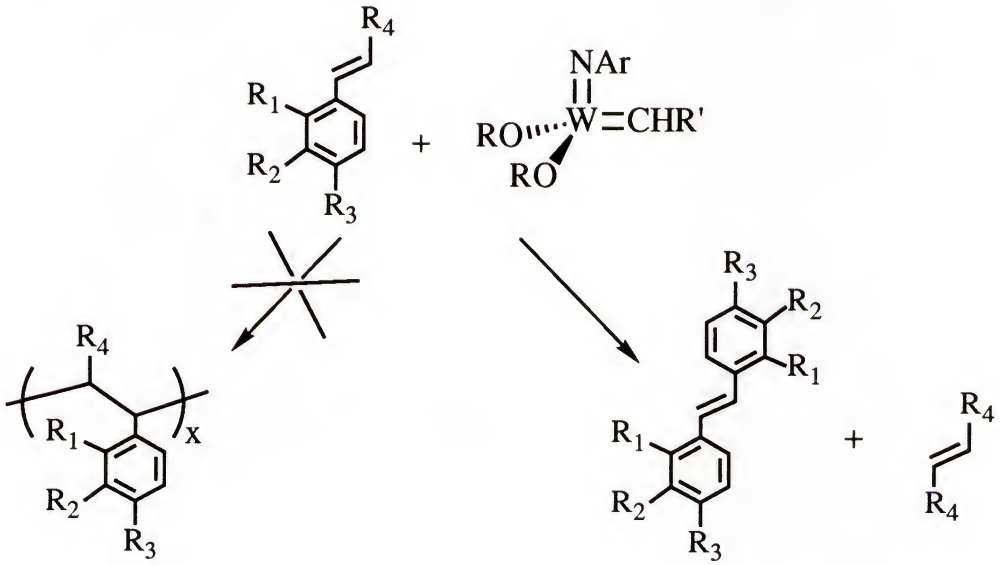


Figure 1.41. Lewis acid free catalyst obviates cation formation, where numbered substitutions represent various halogens or methyl.

These results began a comprehensive investigation as to the precise synthetic rules that govern ADMET. Lewis acid free Schrock alkylidenes provided the means by which successful ADMET polymerization could be achieved. The first high molecular weight polymer was produced by the ADMET condensation of 1,9-decadiene to polyoctenamer (Figure 1.42.1).[232,233] This polymer, which was well known from the ring opening metathesis polymerization of cyclooctene,[169] served as a launching point for Wagener and coworkers who then persisted in demonstrating that an assortment of acyclic dienes were amenable to this new method (Figure 1.42).[234] Polymers which were difficult to prepare by ROMP were soon easily obtained via ADMET chemistry. Exclusively 1,4-polybutadiene, which by ROMP requires cyclobutene or cyclooctadiene, is easily produced from the metathesis condensation of 1,5-hexadiene (Figure 1.42.2).[235]

Random copolymers could also be produced by this new equilibrium method.[236,237] Copolymers containing octenylene and butenylene linkages in a statistical array based on feed ratio resulted from the co-condensation of the two respective monomers or by the reaction of diene with unsaturated polymer.[236] Structure reactivity relationships of monoene and diene hydrocarbons began to develop from the work of Wagener and Konzelman (Figure 1.42).[238,239] Substituent effects were shown to dictate the polymerizability of monomers and in some cases selective polymerization of specific olefins in the monomer resulted in what appears as perfectly alternating copolymers (Figure 1.42.12-14).[238,239] These beginnings established a new direction for Schrock-type alkylidenes of which the tungstalkylidene was used first in exploring hydrocarbon polycondensation as well as other aromatic[237] and ferrocene[240] containing polymers.

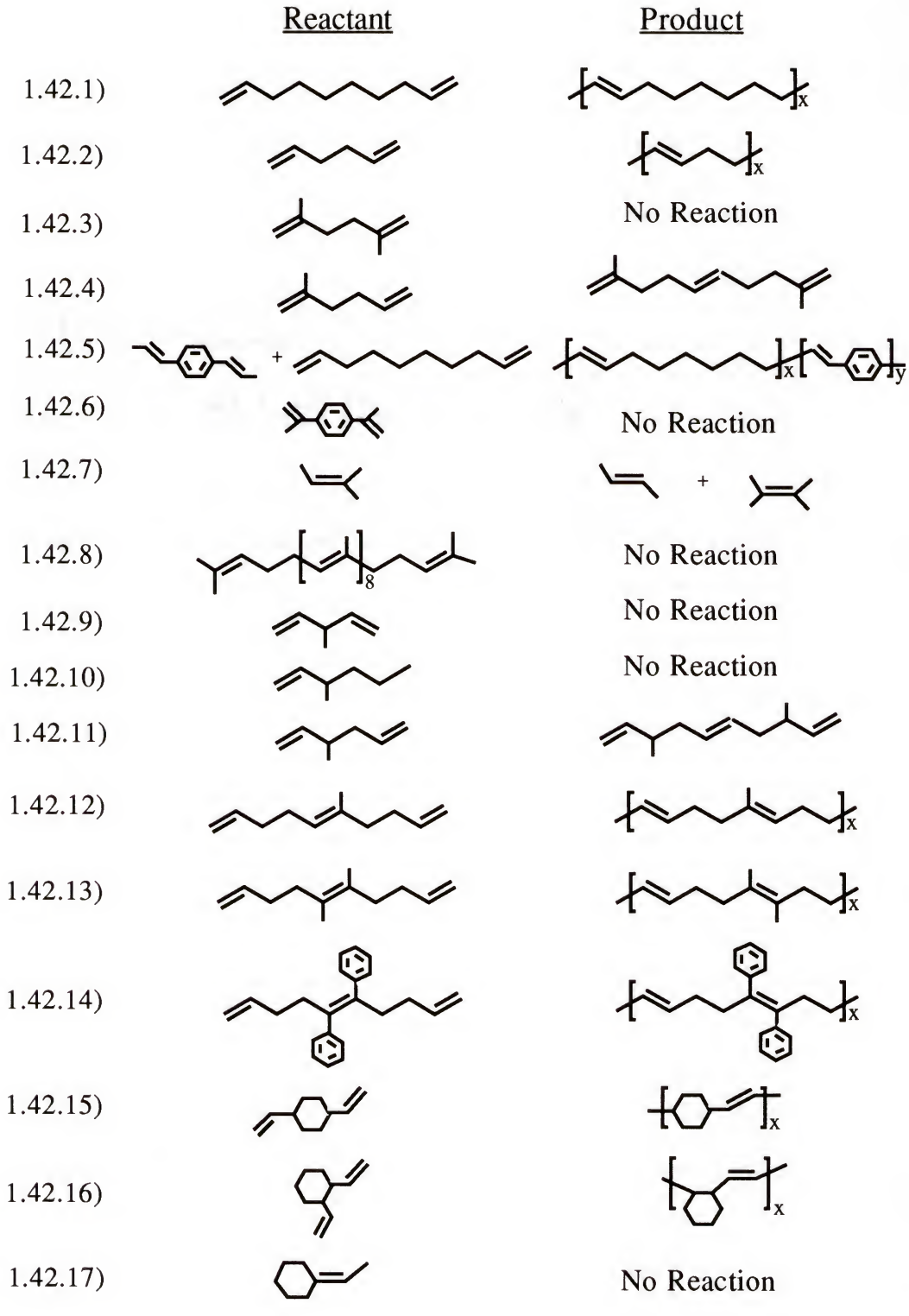


Figure 1.42. ADMET unsaturated hydrocarbon polymers and model studies.

The mechanism of acyclic diene metathesis (ADMET) polymerization (Figure 1.43) contains similar intermediates as does ROMP chemistry.[235] The major difference is that ADMET is an equilibrium process driven by condensation and ROMP propagates irreversibly due to the high reactivity of the alkylidene with strained cycloalkenes. Therefore, ROMP is much faster than ADMET simply because competing equilibria, absent during ROMP, decrease the net productive rate in ADMET chemistry.

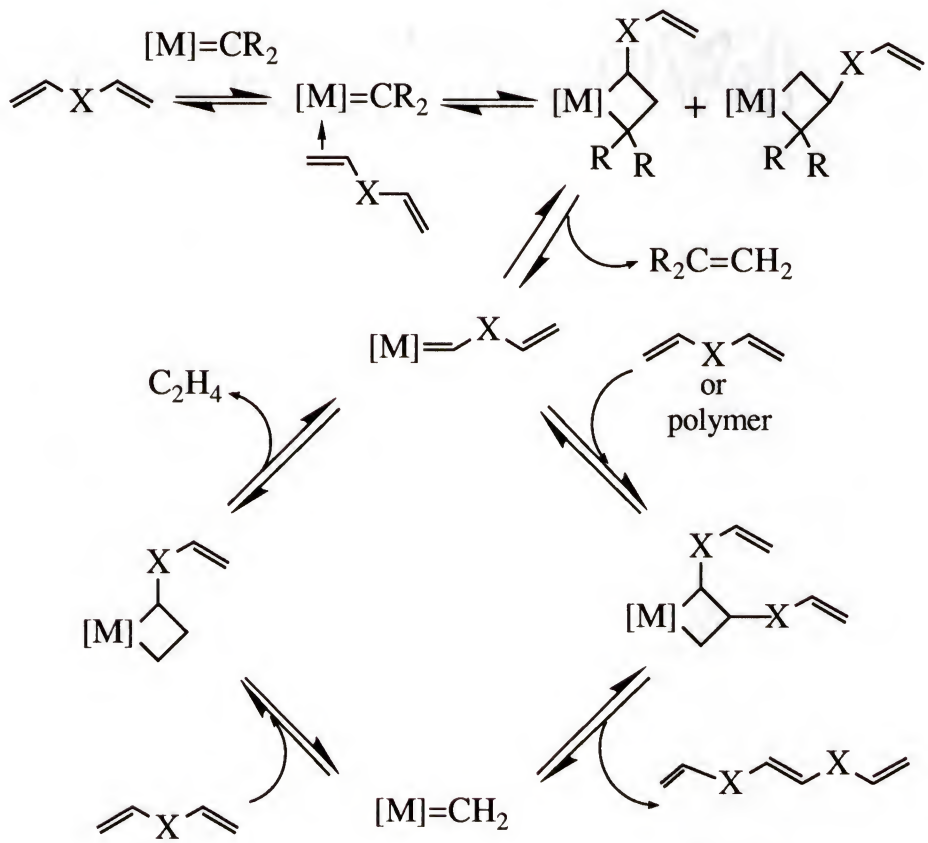


Figure 1.43. Mechanism of acyclic diene metathesis (ADMET) polymerization.

Studies involving the specific exchange mechanisms,[187,194] as well as theoretical calculations[241-243] of olefin metathesis reactions, generally agree that the mechanism begins with π-coordination of the nucleophilic olefin to the electrophilic metal as shown for a general diene in Figure 1.43. Olefin

coordination is well known in organometallic chemistry and many of these complexes have been isolated and characterized.[244]

From the proposed ADMET mechanism (Figure 1.43),[235] the olefin metal complex then collapses via a retro electrocyclic-like reaction forming two possible metallacyclobutane adducts of which only the α,α'-disubstituted metallacycle leads to the productive intermediate as shown in Figure 1.43. Productive cleavage of the metallacycle results in a new alkylidene containing monomer while extruding the former alkylidene ligand as an alkene. This new alkylidene then complexes to monomer forming the α,β-disubstituted metallacycle (only productive metallacycles shown) where non-degenerate retro-complexation results in dimer and the true regenerating catalytic species, a metallamethylidene, when using divinyl monomers. The cycle continues by again adding monomer (or oligomer) producing a monosubstituted metallacycle which cleaves productively to give ethylene and a terminal alkylidene. While the terminal alkylidene is potentially contained within many equilibria, the extent to which they affect polymerization depends greatly on monomer structure, conversion, and reaction conditions, the details of which will be discussed in subsequent chapters. Nevertheless, all ADMET equilibria contain a terminal alkylidene which together with terminal olefin, is required for propagation.

The ADMET mechanism proposed by Wagener, Boncella, and Nel stands as a reliable rationalization of the process based not only on experimental and theoretical precedent yet from certain fundamental and consistent evidence produced from the polymerizations. Some early support for this mechanism includes the fact that ethylene is continuously produced when divinyl monomers are polymerized, and molecular weight distributions (M_w/M_n) of polymers prepared via ADMET approach two, as predicted for step polymerizations. The average geometric configuration of ADMET polymers also increases in *trans*

content as the reaction proceeds which is indicative of a dissociated "non-living" catalysis.[231-235] Furthermore, the equilibrium cycle shown in Figure 1.43 is truly reversible since depolymerization of various high molecular weight unsaturated polymers has been shown to occur, quite efficiently, when excess ethylene is returned to the system.[245]

As is the case for functional ROMP monomers, the molybdenum based catalyst was eventually found to be more tolerant to functionalized dienes than is the tungsten analog. However, initial studies on functional ADMET polymerizations were begun concurrent to the development of Schrock's molybdalkylidene catalyst and were carried out using the tungstalkylidene. Bauch *et al.*[246] began the research by demonstrating that ethylene diundecenoate undergoes ADMET oligomerization before reacting in a Wittig-like manner producing the inactive tungsten-oxo species. These results represented the first evidence that ADMET polymerization of polar functional monomers was possible if the olefin was sufficiently separated from the functionality. Apparently, metathesis is the preferred reaction, initially at least, vs. Wittig chemistry and if coordination into the metallacycle, as previously documented by Schrock and co-workers,[190] can be discouraged by mere separation, then polymerization is possible. Similarly, Brzezinska and Wagener[247-249] discovered that these ideas could be effectively applied to a series of ether containing dienes. Using the tungstaneopentylidene catalyst (1 in Figure 1.31) that previously proved successful for Bauch,[246] and later employing the molybdenum analog,[249] Brzezinska developed the ADMET synthesis rules for acyclic diene ethers (Figure 1.44).

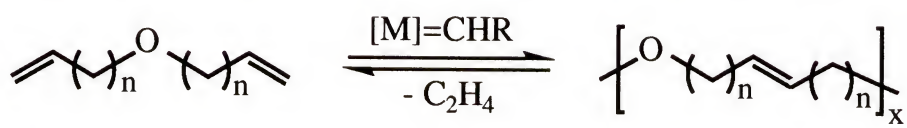


Figure 1.44. ADMET polymerization of diene ethers, where n=1-4.

Divinyl ether (n=0) and diallyl ether (n=1) do not polymerize via metathesis condensation when catalyzed by the tungstaneopentylidene (W=CH-*t*-Bu(N-2,6-C_6H_3-*i*-Pr_2)[OCMe(CF_3)$_2$]$_2$), whereas di-*n*-butyenyl ether (n=2) exhibits only short lived catalytic condensation. However, when the olefin was separated from the electron donating oxygen by four or more methylene spacers, ADMET polymerization occurred readily producing new thermally stable unsaturated polyethers[247] which could be easily modified.[248] Similar results were found when using the molybdeunum alkylidene, Mo=CH-*t*-Bu(N-2,6-C_6H_3-*i*-Pr_2)[OCMe(CF_3)$_2$]$_2$, for these ether dienes, yet diallyl ether did react with this more functionally tolerant catalyst to yield an equilibrium mixture of 2,5-dihydrofuran and linear oligomers. The same equilibrium mixture was also observed when reacting the pure cyclic product, 2,5-dihydrofuran, with the molybdenum catalyst.[249]

The ADMET polymerization of functional dienes received a vigorous start with the work described above and with the advent of Schrock's molybdalkyladiene and the realization that this catalyst was much more tolerant to polar groups, functionalized dienes containing carbonyl groups were soon investigated (Figure 1.45).

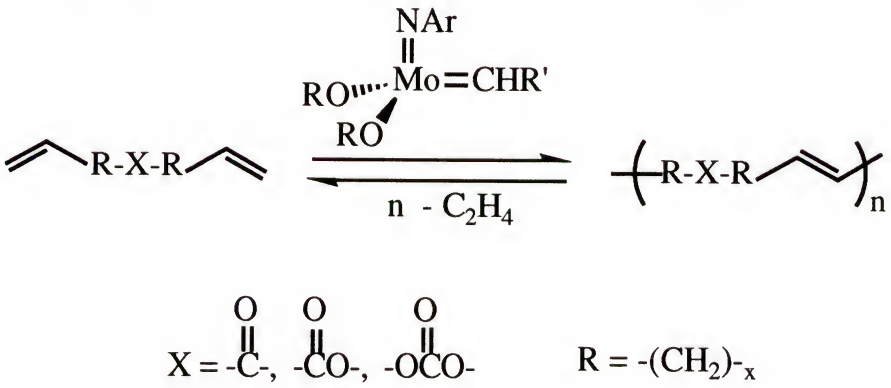


Figure 1.45. ADMET polymerization of carbonyl containing dienes.

The structure/reactivity relationships for dienes containing esters,[197] carbonates,[250] and ketones[251] were developed very recently by Patton .[252] As with previous work, subtle design in monomer drastically affected reactivity, and various new unsaturated polymers and copolymers containing these groups were prepared (Figure 1.45).

While these polar groups affect metathesis catalysis electronically, monomer structural effects of a steric nature are confronted in this dissertation. In an effort to synthesize new and interesting silicon containing polymers, the proximity of alkyl substituents in relation to the polymerizable olefin are shown to play an important role in the development of the synthesis rules and structure/reactivity relationships thereof.

CHAPTER 2

EXPERIMENTAL

Instumentation and Analysis

^{1}H NMR 200 MHz, ^{13}C NMR 50 MHz, and ^{29}Si NMR 40 MHz spectra were obtained with a Varian XL-Series NMR Superconducting Spectrometer system. Chloroform-*d* ($CDCl_3$) or benzene-d_6 was used as solvent and all chemical shifts reported are internally referenced to tetramethylsilane (TMS), $CDCl_3$, or benzene. Heteronuclear gated decoupling was used to supress the NOEs while obtaining quantitative ^{13}C NMR spectra. The spectra were run for 8-14 h with a pulse delay of 10-20 s, and number average molecular weights (M_n) were determined by integrating terminal olefin carbon signals vs. internal olefin carbon signals. Carbon relaxation times (T_1) were determined by standard methods.[253] A heteronuclear gated decoupling pulse sequence with a pulse delay of 10 s was used to obtain ^{29}Si NMR spectra. Infrared analyses were performed on neat oils between NaCl plates with a Perkin Elmer 2 Infrared Spectrophotometer. Ultraviolet analyses were performed on THF solutions (10^{-5} M) with a Perkin-Elmer 9 Spectrophotometer. Mass spectroscopy data--electron impact (EI) or chemical ionization (CI) as indicated--were obtained with a Finnigan 4500 Gas Chromatograph / Mass Spectrometer. High resolution mass spectral data with statistical analysis for molecular formula are reported to the fourth decimal place.

Ethylene samples were collected from the polymerization reactions by condensation with liquid nitrogen, in a 100 ml evacuated flask equipped with a Rotoflow™ high vacuum stop cock and a Suba Seal™ septum. Samples were syringed directly from the pressurized flask. Other non-monomer volatiles were condensed in the same manner under vacuum (~10^{-6} mmHg) and dissolved in chloroform and injected for GC/MS an analysis.

Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Gel permeation chromatography (GPC) data were collected using a Waters Associates Liquid Chromatograph apparatus equipped with a U6K injector and differential refractometer and a Perkin-Elmer LC-75 ultraviolet (UV) spectrophotometric detector. Two Phenomenex 7.8 mm x 30 cm Phenogel 5 consecutive linear cross linked polystyrene gel columns were used; a 500 Å followed by a 1000 Å type. The eluting solvent was HPLC grade tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. Filtered (~50 μm) polymer samples were dissolved in THF (0.2-0.5 % w/v) and injected (10-40 μL). Retention times were calibrated against polystyrene standards (Scientific Polymer Products, Inc.) or polybutadiene standards (Polysiences, Inc.) as indicated in the text. The following polystyrene molecular weight standards of known polydispersity were used : M_W = 110000, 39000, 7820, 4000, and 1152 and where $M_W/M_n \leq 1.06$. The following polybutadiene molecular weight standards of known polydispersity were used : M_W = 110000, 24000, 2760, 982, and 439 and where $M_W/M_n \leq 1.07$.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) data were obtained with a Perkin Elmer 7 Series Thermal Analysis System or from a Dupont 2000 (DSC 2910 and Hi-Resolution TGA 2950) Thermal Analysis System. DSC samples (10-20 mg) were analyzed with liquid nitrogen as coolant under a helium or nitrogen flow at a rate of 25 mL/min. Polycarbosilane homopolymer samples were cycled from -100 to 40 °C at successive decreasing

scan rates ranging from 20 to 5 °C/min. The polycarbosilane copolymer (10) was cycled from -100 to 80 °C at decreasing scan rates ranging from 20-1 °C/min. Polycarbosiloxane samples were annealed at 200 °C and quenched to -150 °C, then cycled from -150 to 150 °C at successive decreasing scan rates ranging from 10-1 °C/min. TGA samples were performed under nitrogen and air with a flow rate of 50 mL/min and program heating from 50 to 700 °C at a rate of 10 °C/min.

Materials and Techniques

The Lewis acid free catalysts used in the polymerizations, $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)M{=}CHC(CH_3)_2R$, where M = W[187] (1a,b in Figure 3.1) or Mo[194] (1c in Figure 3.1) and R= CH_3 (neopentyl) or Ph (neophyl) were generously provided by Professor J.M. Boncella, Dr. A.S. Gamble, Dr. C. Bauch, Dr. J.T. Patton, and J. Konzelman at the University of Florida during the completion of this work. The catalyst were prepared by known published methods developed by Schrock *et al.*[186-190,194] A silicone oil diffusion pump coupled with a mechanical pump (10^{-5} mmHg) high vacuum mainifold system 10^{-6} mmHg) was used for catalyst and volatile monomer manipulations. Catalyst was introduced by either adding to pure monomer under nitrogen in a glove box, vacuum transferring monomer into an evacuated vessel containing catalyst or by utilizing breakseal techniques under high vacuum.[232,235] Breakseals were prepared by dissolving the pre-weighed (20 mg) catalyst in pentane, syringing into high vacuum Rotoflow™ valve equipped breakseal ampules, evaporating to remove all solvent, sealing in vacuo with a methane/oxygen torch and storing in the dark below 0 °C.

All volatile monomers were fractionally distilled from CaH_2, degassed under high vacuum by several freeze-thaw cycles, then vacuum transferred to a

potassium or sodium mirror successively until no reaction was observed, then vacuum transferred directly into the reaction flask, breakseal ampule or Rotoflow™ equipped storage flask. On occasion, treatment with catalyst for purification was necessary. Diallyldimethylsilane (3) (Aldrich), dimethyldivinylsilane (2) (Hülls-Petrarch), 1,9-decadiene (9) (Aldrich), and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Hülls-Petrarch), were purchased and purified in this manner. Allylchlorodimethylsilane (Aldrich) and allyldimethylsilane (Hülls-Petrarch) were purified as above without the use of CaH_2 or a potassium mirror. Toluene and pentane were deolefinated by extracting with cold concentrated H_2SO_4 followed by basic $KMnO_4$. These solvents as well as all other reaction solvents, such as THF, were dried by refluxing over sodium / potassium benzophenone ketyl before distilling under argon. Bis(dimethylhydroxysila)benzene, dichlorosilanes, dichloro(-2n-methyl)-n-siloxanes (all obtained from Hülls-Petrarch), and 1,4-pentadiene (99 %, Aldrich) were purchased and used as received Tetramethyldisiloxane and tris(divinyltetramethyldisiloxane)Pt_2(0) (Karstedt's catalyst)[254] were obtained from Rhone-Poulenc Centre de Recherches St. Fons, France. 4,4'-Bis(*trans*-1-propenyl)biphenyl (30) was generously donated by J.M. Boncella and A.S. Gamble, Department of Chemistry, University of Florida. All other reagents were purchased and used as received.

Polymerizations were conducted by one of two techniques as indicated. Volatile monomers were polymerized in a flame dried custom ADMET apparatus[232,235] equipped with a dry ice / isopropanol condenser and an ethylene collection flask separated by a high vacuum Rotoflow™ valve under a vacuum of 10^{-6} mmHg. Less volatile monomers and all dimerization or model studies were reacted in a 50 - 100 mL round bottom flask equipped with a high vacuum Rotoflow™ valve.

Synthesis and Characterization

Attempted Polymerization of Divinyldimethylsilane (2) with Catalyst 1. The following general procedure was used for the attempted polymerization of monomer 2. To a flame dried custom ADMET apparatus equipped with stir bar and under a vacuum of 10^{-6} mmHg was added via breakseal techniques $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2M{=}CHC(CH_3)_2R$ (1a-c as defined by Figure 3.1), (1 eq) and 3-5 mL (500-1000 eq) of dimethyldivinylsilane (2) at room temperature. The mixture was stirred for several hours at room temperature with no obvious indication of reaction (ethylene was not observed). The clear, light yellow solution was heated to 45 °C and allowed to stir for several hours and then at room temperature for several days. In another similar experiment the reaction was cooled to -78 °C and allowed to warm slowly to room temperature. In every case--regardless of the catalyst used--pure starting material (2) was recovered and no new products were detected by ^1H or ^{13}C NMR.

Synthesis of (4,4,7,7-Tetramethyl)-4,7-disiladeca-1,9-diene (5). Monomer 5 was prepared by the slow addition of allylmagnesium chloride (1 M in diethylether) (2.1 eq.) over 30 min to a THF solution (1.1 M after addition) of 1,1,4,4-tetramethyl-1,4-dichlorodisilethylene (Petrarch) (1 eq) followed by strong reflux for 14 h. The reaction was quenched with aqueous $NaHCO_3$ (5 g/L), extracted with diethylether, dried and fractionally distilled from CaH_2 at 60 °C (3.5 mmHg) to give the clear liquid product in 82 % yield. The monomer was stirred on a potassium mirror, vacuum transferred to a breakseal ampule, and sealed. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$), δ

-0.19 (s, 12H), 0.20(d, 4H), 1.34(d, 4H), 4.64(m, 4H), 5.56(sept, 2H, J = 7Hz); ^{13}C NMR (50 MHz, CDCl3), d -4.29, 6.72, 22.73, 112.58, 135.15; ^{29}Si NMR (40 MHz, $CDCl_3$), δ 3.05. Anal. Calcd for $C_{12}H_{26}Si_2$ gave: Calc.(Found) C 63.61(63.36), H 11.59(11.63).

Synthesis of Bis-1,4-(diallyldimethylsilyl)benzene (7). Monomer 7 was prepared by the "in situ" Grignard reaction of 1,4-dibromobenzene (1.0 eq) with magnesium powder (2.2 eq.) and allylchlorodimethylsilane (2.0 eq) in refluxing THF. 1,4-dibromobenzene was stirred at room temperature in THF with Mg powder (1.1 eq) and catalytic iodine with periodic heating with a heat gun for 5 h. The solution was then added via cannula to allylchlorodimethylsilane (0.7 M in THF) (2.0 eq) and allowed to stir at room temperature for 18 h, after which another addition of Mg powder (1.1 eq.) (0.3 M in THF) was added and the mixture was refluxed for 51 h. The reaction was quenched with aqueous $NaHCO_3$ (5 g/L), extracted with diethylether, dried and distilled at 90-100 °C (10^{-6} mmHg) to give the clear liquid product in 37 % isolated yield. The monomer was stirred over a sodium mirror, vacuum distilled to a breakseal ampule and sealed. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$), δ 0.18(s, 12H), 1.61(d, 4H), 4.86(m, 4H), 5.80(sept, 2H, J = 7Hz), 7.54(s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$), δ -3.54, 23.58, 113.43, 132.84, 132.88, 139.99; ^{29}Si NMR (40 MHz, $CDCl_3$), δ -4.77. Anal. Calcd for $C_{16}H_{26}Si_2$ gave: Calc.(Found) C 69.98(69.98), H 9.56(9.58).

Synthesis of Poly(1,1-dimethyl-1-silapent-3-ene) (4). To a flame dried custom ADMET apparatus equipped with stir bar and under a vacuum of 10^{-6} mmHg was added via breakseal techniques $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2W{=}CHC(CH_3)_3$ (1a), (20 mg, 1 eq) and 5 ml (1000 eq) of

diallyldimethylsilane (3) at room temperature. The solution was slowly heated to 45 °C at which time began a rapid evolution of ethylene. Ethylene was collected and an increase in viscosity was noted within 30 min. When viscosity increased to a point as to hinder stirring, the temperature was increased to 50 °C and stirring continued for 74 h under full vacuum. During this time, solid white volatiles were collected and upon analysis were shown to be the cyclic dimer (27). After exposure to the atmosphere, the reaction contents were dissolved in CCl_4 and washed with methanol to give 85 % isolated yield of opaque viscous polymer. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$), δ -0.04(s, 6H), 1.41(d, 4H), 5.20(*trans*)(t, br), 5.28(*cis*)(t, br, 2H); ^{13}C NMR (50 MHz, $CDCl_3$), δ -3.41(*cis*), -3.86(*trans*), 16.26(*cis* allylic), 20.99(*trans* allylic), 123.03(*cis*), 124.31(*trans*); ^{29}Si NMR (40 MHz, $CDCl_3$), d 0.756(*trans*), 1.512(*cis*). IR υ 1637(s, C=C), 1630(w, allylSi), 1260(st, br, SiMe), 1150cm^{-1}. Anal. Calcd for $C_6H_{12}Si$ gave: Calc(Found) C 64.18(64.26), H 10.80(10.81).

Synthesis of Poly(1,1,4,4-tetramethyl-1,4-disilaoct-6-ene) (6). Polymer 6 was prepared by a similar procedure described for 4 above in 79 % isolated yield after purification. Monomer 5 was treated with $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHC(CH_3)_2Ph$ (1b) as purification and vacuum transferred to a breakseal ampule. Upon second contact with catalyst 1b, the mixture immediately began to froth rapidly with the evolution of ethylene. Viscosity quickly increased and heating was required for consistent stirring. After 21 h, trace liquid volatiles were collected and upon analysis were shown to be the cyclic monomer (28). Stirring continued for 72 h at 50 °C under full vacuum. The polymer was dissolved in CCl_4 and precipitated in methanol. Due to its viscous oily nature, centrifugation was necessary to isolate the polymer. The clear viscous polymer was dried under high vacuum. It had the following spectral properties. ^1H NMR (200 MHz,

$CDCl_3$), δ -0.06(*trans*), -0.04(*cis*)(s, 12H), 0.39(d, 4H), 1.39(d, 4H), 5.18(*trans*), 5.27(*cis*)(t, 2H); ^{13}C NMR (50 MHz, $CDCl_3$), d -4.10(*trans*), -3.88(*cis*), 7.04, 16.07(*cis* allylic), 20.87(*trans* allylic), 123.17(*cis*), 124.39(*trans*); ^{29}Si NMR (40 MHz, $CDCl_3$), δ 3.181(*trans*), 3.966(*cis*). IR υ 1637(s, C=C), 1260(st, br, SiMe), 1150 cm^{-1}. Anal. Calcd for $C_{10}H_{22}Si_2$ gave: Calc(Found) C 60.50(60.31), H 11.19(11.18).

Synthesis of Poly(1-(1,1-dimethylsila)-4-(1,1-dimethylsilapent-3-ene)phenylene) (8). Polymer 8 was prepared similarly as above except $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHC(CH_3)_2Ph$ (1b, 1 eq) was washed down the inside of the ADMET flask with toluene which was then removed in vacuo. Monomer 7 (500 eq) was added via breakseal techniques and upon contact with catalyst, vigorous release of ethylene occurred. An increase in viscosity was noted after 30 min. The polymer was allowed to stir at 50 °C for 23 h until no further ethylene was produced then was exposed to the atmosphere. The opaque, viscous polymer was dissolved, washed and isolated as before in 74% isolated yield. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$), δ 0.25(m, 12H), 1.65(m, 4H), 4.69(m, terminal CH=), 5.33(m, 2H), 5.57(sept, terminal $=CH_2$), 7.50(m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$), δ -3.25, 16.85(*cis* allylic), 21.75(*trans* allylic), 23.41(terminal allylic), 113.23(terminal $=CH_2$), 123.37(*cis*), 124.58(*trans*), 132.86, 132.90, 139.85(terminal CH=); ^{29}Si NMR (40 MHz, $CDCl_3$), d -2.515, -1.279. IR υ 1637(s), 1630(s, allylSi), 1420(s, SiPh), 1250(st), 1135(s,st, SiArSi) cm^{-1}. Anal. Calcd for $C_{14}H_{22}Si_2$ gave: Calc(Found) C 68.52(67.61), H 9.11(8.43).

Synthesis of Poly(1,1-dimethyl-1-silapropene)co-octenamer (10). Copolymer 10 was prepared by stirring, under the conditions described above,

dimethyldivinylsilane (2) (0.05 mol, 2000 eq) with $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHC(CH_3)_2Ph$ (1b, 1 eq.) for 3 h at 40 ° C then at room temperature for 111 h. 1,9-decadiene (9) (0.05 mol, 2000 eq) was then added followed by an immediate evolution of ethylene and a viscosity increase within 30 min. The mixture was stirred at 50 °C for 5 days. The copolymer was washed and precipitated from methanol as a white powder in 77 % isolated yield. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$), δ 0.04 - 0.28(five SiMe signals, sh), 1.30(s, broad), 1.98(s, broad), 5.38(m, broad), integration gives a 1:21:10:5 respective ratio (approx. 6 mol% dimethyldivinylsilane silane repeat unit). Attached proton test (APT) ^{13}C NMR (50 MHz, $CDCl_3$), δ -2.83, -2.35, -1.44, -0.979, 0.354 (Si*Me*), 27.19(*cis* internal octenamer allylic), 29.06, 29.64, 32.60(*trans* internal octenamer allylic), 33.70(terminal octenamer allylic), 36.75(vinylsilane allylic), 114.12(terminal octenamer $=CH_2$), 126.42, 127.35, 128.10, 128.29, 128.66(terminal divinyl silane CH=), 129.81(*cis* internal octenamer), 130.29(*trans* internal octenamer), 131.27(*cis* terminal vinylsilane $=CH_2$), 131.62(*trans* terminal vinylsilane $=CH_2$), 139.20 (terminal octenamer CH=), 147.77, 148.19, 148.75, 149.42, 149.82, 150.41(internal vinylsilane). Quantitative ^{13}C NMR integration also gave approx. 6 mol% dimethyldivinylsilane silane repeat unit. IR υ 1600(s, sh), 1640(m), 1490(s), 1260(s,sh, SiMe) cm^{-1}.

Reaction of Divinyldimethylsilane (2), with Catalyst 1b. To an NMR tube, under a dry and inert atmosphere, was added 1.5 mL benzene-d_6 and 20 mg (0.02 M, 1 eq.) of tungsten alkylidene 1b ($PhMe_2CCH{=}W(NAr)\text{-}[OCMe(CF_3)_2]_2$). 100 μL (0.4 M, 28 eq.) of divinyldimethylsilane was then added and the solution was capped and analyzed immediately by ^1H and ^{13}C NMR spectroscopy. The following resonances, indicative of $W[CH(SiMe_2CH{=}CH_2)CH(SiMe_2CH{=}CH_2)]$-

(NAr)[OCMe(CF_3)$_2$]$_2$ (11) were found (excess divinyldimethylsilane resonances are omitted): ^{1}H NMR (200 MHz, C_6D_6), δ -0.06(m, β-C*H*SiMe$_2$CH=CH$_2$), -0.15, 0.53, 0.45, 0.06(Si*Me*$_2$ CH=CH$_2$), 1.26 (m, CH*Me*$_2$), 1.66, 1.81(s, OC*Me*(CF_3)$_2$), 4.05(m, C*H*Me$_2$), 4.12(m, α-C*H*SiMe$_2$CH=CH$_2$), 4.51(dd, J = 5 and 9, α-CH$_2$, other α-H not resolved), 6.79 (ArH_p), 6.97(ArH_m). ^{13}C NMR (CF_3 and aryl carbon signals omitted), (50 MHz, C_6D_6), δ -2.7, -1.6, -1.1, -0.03(Si*Me*$_2$ CH=CH$_2$), 4.6(β-*C*HSiMe$_2$CH=CH$_2$), 18.3, 19.0 (OC*Me*(CF_3)$_2$), 24.3, 24.7, 26.4, 27.5(CH*Me*$_2$), 27.6, 28.2(*C*HMe$_2$), 104.3(α-*C*HSiMe$_2$CH=CH$_2$), 110.8(α-CH$_2$).

Reaction of 1,9-Decadiene (9) with Monomer 2 and Tungstacycle 11. 100 μL (23 eq.) of 1,9-decadiene was added to the solution above and immediately analyzed by ^{1}H and ^{13}C NMR spectroscopy. New signals, other than 1,9-decadiene, were not observed in the NMR spectra upon addition. The mixture was heated to 42 °C for 48 hours whereafter, the following new resonances corresponding to 1,9-decadiene metathesis condensation and ethylene were evident: ^{1}H NMR (200MHz, C_6D_6), δ -0.89(m, β-C*H*), 3.99(m, C*H*Me$_2$), 4.46(m, α-C*H*), 5.33(C$_2$*H*$_4$), 5.52(-C*H*=C*H*-). ^{13}C NMR (50 MHz, C_6D_6), δ 1.26.8, 126.4, 126.1(=*C*HSi-), 130.2(*cis*-*C*H=*C*H-), 130.7(*trans*-*C*H=*C*H-), 131.6, 132.0(-SiCH=*C*H$_2$), 126.8, 126.4, 126.1(=*C*HSi-).

Reaction of 1,4-Pentadiene with Catalysts 1b and 1c. In a typical reaction, 1,4-decadiene (3 mL, 2000 eq) was added (neat or with 1-2 mL dry benzene), under an inert atomosphere, to alkylidene catalyst PhMe$_2$CCH=M(NAr)[OCMe(CF_3)$_2$]$_2$, M = W (1b), Mo (1c), (10 mg, 1 eq) in a Schlenk tube with stirring. The mixture was allowed to stir under an inert atmosphere for several hours and analyzed by NMR. Catalyst 1b did not condense

ethylene, as observed by ^1H NMR, yet the molbdenum catalyst, 1c, produced 1,4-cyclohexadiene in 9.1 % conversion. It had the following spectral properties: ^1H NMR (200 MHz, $CDCl_3$), δ 2.8(m), 5.49(t, =C*H*); ^{13}C NMR (50 MHz, $CDCl_3$), δ 37.84, 136.40. Mass spectral (EI) data for C_6H_8 = 80.14 g/mol: M/Z = 80.

Reaction of Allylchlorodimethylsilane with Catalyst 1b and 1c: Synthesis of Bis(chlorodimethylsilyl)-2-butene (12). In a side by side experiment, pure allylchlorodimethylsilane (2 mL, 1023 eq) was added each to two vials under an inert atmosphere. To one was added catalyst 1b (1 eq) and to the other was added the molybdenum catalyst 1c (1 eq), where $PhMe_2CCH{=}M(NAr)[OCMe(CF_3)_2]_2$, M = W (1b), Mo (1c). The vials were shaken and allowed to stand for 48 h where upon analysis catalyst 1b had produced 12 to a maximum 88 % (66 % *trans*) and catalsyt 1c failed to react. In another experiment, catalyst 1c converted allychlorodimethylsilane to 65 % 12 in 1 h and then slowly to a maximum 91 % (59 % *trans*) 12 after several weeks. Compound 12 had the following spectral properties: ^1H NMR (200 MHz, $CDCl_3$), δ 0.43 (s, 12H), 1.75 (m, 4H), 5.34 (m, -C*H*=, *trans*), 5.44 (m, -C*H*=, *cis*); ^{13}C NMR (50 MHz, $CDCl_3$), δ 1.20, 24.88, 12268 (*cis*); 123.98 (*trans*). HRMS (EI): M/Z, 241.0296, Calcd for $C_8H_{18}Si_2Cl_2$, 240.0324.

Reaction of Allyldimethylsilane with Catalyst 1c: Synthesis of Bis(dimethylsilyl)-2-butene (13). Allyldimethylsilane (3mL, 1600 eq) was purified by distillation from CaH_2 and degassed. Molybdenum catalyst 1c (1 eq) was added under an inert atmosphere at room temperature whereupon addition ethylene evolved. The reaction was allowed to stir for 30 h to give a maximum 49 % (75 % *trans*) of the dimer 13. It had the following spectral properties: ^1H NMR (200 MHz, $CDCl_3$), δ 0.09, 0.11 ($SiMe_2$), 1.50 (m, allylic), 3.88 (m, Si-H),

5.28 (m, -C*H*=, *trans*), 5.36 (m, -C*H*=, *cis*); ^{13}C NMR (50 MHz, $CDCl_3$), δ -4.86, -4.53, 15.31, 19.14, 123.25 (*cis*); 124.60 (*trans*). HRMS (EI): M/Z, 172.1102, Calcd for $C_8H_{20}Si_2$, 172.1104.

Synthesis of 1,3-Bis(vinyl)-1,3-dimethyldisiloxane (14). Divinyldisiloxane 13 was prepared by the hydride reduction of the corresponding dichlorosiloxane. To a solution (0.1 M in THF) of lithium aluminum hydride (LAH) (0.1 mol), under Ar and cooled to -78 °C was added, 1,3-dichloro-1,3-dimethyl-1,3-divinyldisiloxane (0.11 mol) in two additions over 30 min. The mixture was allowed to warm to room temperature and stir for 12 h under Ar. The product and solvent was then slowly high vacuum distilled at room temperature, filtered over celite under Ar, and concentrated under reduced pressure to give 14 as a clear liquid in 48 % isolated yield. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$), δ 0.255(d, 6H, J = 3.5 Hz), 4.72 (m, 2H, -SiMe*H*), 5.88 (m, 1H), 6.07 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$), δ 1.01, 133.83, 136.81. Mass spectral (EI) data for $C_6H_{14}OSi_2$ = 158.37 g/mol: M/Z = 157.

Reaction of Bis(vinyl)dimethyldisiloxane (14) with Catalyst 1c. To pure molybdenum catalyst 1c (10 mg, 1 eq) was added under high vacuum and at -197 °C, divinylsiloxane 13 (1.5 ml, 730 eq) under high vacuum (10^{-5} mmHg). The mixture was allowed to warm slowly over a period of 5 h to -30 °C and stir for 2 h with intermittent vacuum before warming to room temperature and stirring for an addtional 12 h. The products were undefined, yet the following new resonances indicative of metathesis condensation were observed: ^1H NMR (200 MHz, C_6D_6), δ 0.35(m), 5.1 (m, -SiMe*H*), 5.85-6.4 (br m); ^{13}C NMR APT (50 MHz, $CDCl_3$), δ -0.1, 128.0 (=CH-), 135.6 (=CH_2), 136.7 (=CH-).

Synthesis of 1,3-Bis(allyl)-1,1,3,3-tetramethyldisiloxane (15). To a solution of allylmagnesium bromide (200 mL, 0.2 mol, 2.1 eq.), in diethyl ether (1.0 M), under argon at -78 °C was added a solution of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane (18.47 g, 0.091 mol, 1 eq.) in diethyl ether (3.6 M), dropwise over a period of 1 h. An additional 10 mL of dry diethyl ether was added, and the mixture (0.39 M in chlorosilane after addition) was allowed to warm to room temperature and stir for 3.5 h then reflux for 10 h. The mixture was quenched with 100 mL $NaHCO_3$ (sat.), extracted with diethyl ether, dried over anhydrous Na_2SO_4, and the solvent was evaporated giving 15.9 g of the clear liquid 15 in 82 % yield. Diene 15 was purified by distilling from CaH_2 (b.p. = 37-40 °C, 1.0 mmHg), degassing by several freeze-pump-thaw cycles and stirring on a potassium mirror. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.08 (s, 12 H), 1.54 (d, 4 H, J = 8 Hz), 4.82 (m, 4 H), 5.79 (m, 2 H, J = 8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.11, 26.41, 113.31, 134.36. ^{29}Si NMR (40 MHz, $CDCl_3$): δ 5.61. IR: ν 3090 (m, vinyl), 1635 (m, allyl Si), 1260 (s, sh, SiMe), 1065 (s, br, SiOSi) 825 cm^{-1}. Anal. Calcd for $C_{10}H_{22}OSi_2$ (found): C, 55.99 (55.98); H, 10.36 (10.39).

Synthesis of 1,1,3,3-Tetramethyldisiloxacyclohept-5-ene (16). To an evacuated flask containing $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)Mo{=}CHC(CH_3)_2Ph$ (1c)(20 mg, 2.6x10^{-5} mol, 1 eq.) was added in vacuo, pure diene 15 (3.5 g, 0.02 mol, 600 eq.) at liquid N_2 temperature. The mixture was allowed to warm at room temperature, and upon homogeneity (ca. -20 °C) evolution of ethylene began and persisted, increasing in rapidity with temperature, for 40 min. The mixture was allowed to stir for an additional 2 h and then vacuum transferred, yielding the clear liquid, b.p. 60-61 °C (18 mmHg) (lit. 160-163 °C)[256], 16, in 99 % conversion. It had the following spectral properties. ^{1}H NMR

(200 MHz, $CDCl_3$): δ 0.09 (s, 12 H), 1.53 (m, 4 H, $A_2XX'A_2'$), 5.62 (m, 2 H, $A_2XX'A_2'$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.14, 19.70, 124.13. ^{29}Si NMR (40 MHz, $CDCl_3$): δ 8.62. IR: ν 3040 (m, *cis*), 1630 (allyl Si), 1260 (s, sh, SiMe), 1035 (s, br, cyclic SiOSi), 850, 810 cm^{-1}. HRMS (EI): M/Z, 186.0911, Calcd for $C_8H_{18}OSi_2$, 186.0896. Anal. Calcd for $C_8H_{18}OSi_2$ (found): C, 51.54 (51.44); H, 9.75 (9.77).

Synthesis of 1,5-Bis(allyl)-1,1,3,3,5,5-hexamethyltrisiloxane (17). To a solution of allylmagnesium bromide (200 mL, 0.2 mol, 2.2 eq.) in diethyl ether (1.0 M) under argon at -5 °C was added a solution of 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane (20.47 g, 0.09 mol, 1 eq.) in dry THF (3.0 M), dropwise over a period of 1 h. An additional 150 mL of dry THF was added, and the mixture (0.26 M in chlorosilane after addition) was allowed to warm to room temperature and stir for 2 h then reflux for 5 h. The mixture was quenched with 100 mL aqueous $NaHCO_3$ (5 g/L), extracted with diethyl ether, dried over anhydrous Na_2SO_4, and the solvent was evaporated giving 19.90 g of the oil, 17, in 77% yield. Monomer 17 was purified by distilling from CaH_2 (b.p. = 42-43 °C, 5.0 mmHg), degassing by several freeze-pump-thaw cycles and stirring on a potassium mirror. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$): δ 0.03 (s, 6 H), 0.09 (s, 12 H), 1.57 (d, 4 H, J = 8 Hz), 4.87 (m, 4 H), 5.79 (m, 2 H, J = 8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ -0.26, 1.25, 26.29, 113.34, 134.36. ^{29}Si NMR (40 MHz, $CDCl_3$): δ -20.72, 4.12. IR: ν 3095 (m, vinyl), 1634 (m, allyl Si), 1260 (s, sh, SiMe), 1060 (s, br, SiOSi) 825, 800 cm^{-1}. Anal. Calcd for $C_{12}H_{28}O_2Si_3$ (found): C, 49.93 (50.19); H, 9.80 (9.84).

Synthesis of 1,3-Bis(4-pentenyl)-1,1,3,3-tetramethyldisiloxane (19). To a solution of 1,4-pentadiene (10.0 g, 0.147 mol, 2.5 eq.) and

tris(divinyltetramethyldisiloxane)$Pt_2(0)$ (Karsted's catalyst)[254] (1.488 mg of 10.6 % soln. in hexane, 10^{-5} eq.) at 10 °C, under N_2, was slowly added hexamethyldisiloxane (7.89 g, 0.059 mol, 1 eq.) over 40 min. An exotherm was produced, and intermittent cooling with an ice bath was required to keep the solution below 35 °C during the addition. The solution was allowed to stir at room temperature for 42 h under N_2, then fractionally distilled (b.p. = 68 °C (1 mm Hg)) giving the pure β isomer of 19 in 17 % isolated yield. GC indicated that the monomer was produced with 95% β regioselectivity prior to distillation. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$): δ 0.04 (s, 12 H), 0.52 (m, 4 H), 1.41 (m, 4 H), 2.06 (m, 4 H), 4.98 (m, 4 H, $=CH_2$), 5.80 (m, 2 H, -CH=). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.38, 17.95, 22.83, 37.43, 114.40, 139.00. ^{29}Si NMR (40 MHz, $CDCl_3$): δ 8.61. IR: ν 3090 (m, vinyl), 1643 (m, allyl Si), 1255 (s, sh, SiMe), 1060 (s, br, SiOSi) 845, 800 cm^{-1}. HRMS (CI): M/Z, 271.2091, Calcd for $C_{14}H_{31}OSi_2$, 271.1914.

Synthesis of 1,4-Bis(3-allyl-1,1,3,3-tetramethyldisiloxa)benzene (21). To a solution of 1,4-bis(dimethylhydroxysila)benzene (9.45g, 0.042 mol, 1 eq.) in 100 mL dry THF (0.42 M) at 0 °C, was added a solution of allylchlorodimethylsilane (12.36 g, 0.092 mol, 2.2 eq.) in 60 mL dry THF (1.5 M) over a period of 1 h. The solution was allowed to stir at 0-5° C for 1 h and 10 mL pyridine was added whereupon a white solid formed, and the mixture was allowed to warm to room temperature. An additional 100 mL THF was added and stirring continued for 12 h before refluxing for 7 h, cooling to room temperature and filtering over neutral alumina. The residue was washed repeatedly with hexane, and the combined washings were removed from the filtrate in vacuo to give the crude oil in 92% yield. The crude product was dissolved in ether and extracted twice each with sat. Na_2CO_3 soln., brine, and water, then dried over $MgSO_4$ and evaporated to give 21

as a white solid in 61 % isolated yield. Monomer 21 was purified by recrystallization from ethanol, m.p. = 55-60 °C. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.10 (s, 12 H), 0.34 (s, 12 H), 1.59 (d, 4 H, J = 7 Hz), 4.89 (m, 4 H), 5.79 (m, 2 H, J = 7 Hz), 7.56 (s, 4 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.07, 0.89, 26.43, 113.47 (vinyl CH_2), 132.22 (vinyl CH), 134.22 (aromatic CH), 140.94 (ipso). ^{29}Si NMR (40 MHz, $CDCl_3$): δ -21.59, 5.61. IR: ν 3080 (m, vinyl), 3060 (m, aromatic), 1634 (m, allyl Si), 1260 (s, sh, SiMe), 1060 (s, br, SiOSi) 835, 800 (s) cm^{-1}. HRMS (CI): M/Z, 422.1940, Calcd for $C_{20}H_{38}O_2Si_4$, 422.1949. Anal. Calcd for $C_{20}H_{38}O_2Si_4$ (found): C, 56.80 (56.98); H, 9.08 (8.65).

Synthesis of 1,4-Bis(pentamethyldisiloxa)benzene (23). To a solution of 1,4-bis(dimethylhydroxysila)benzene (5.0 g, 0.0221 mol, 1 eq.) in 30 mL dry pyridine at 0 °C, was added chlorotrimethylsilane (9.61 g, 0.0884 mol, 4 eq.) in one addition under Ar. Upon addition a white solid formed immediately and the mixture was allowed to stir at 0-5 °C for 2 h. A distillation head was then attached and the volatiles were removed. The crude product was dissolved in ether and extracted twice each with sat. Na_2CO_3 soln., brine, and water, then dried over $MgSO_4$ and evaporated to give 23 as a clear oil in 65 % isolated yield. 23 was purified by high vacuum distillation, b.p. = 25-30° C (10^{-6} mmHg). It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.10 (s, 18 H), 0.34 (s, 12 H), 7.55 (s, 4 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.07, 0.89, 134.22 (aromatic CH), 140.94 (ipso). HRMS (CI): M/Z, 370.1663, Calcd for $C_{20}H_{38}O_2Si_4$, 370.1636.

Synthesis of Cyclo-1,1',4,4'-bis(1,1,3,3-tetramethyldisiloxa)dibenzene (24). The byproduct 24 sublimed directly from the product mixture of 21 upon heating

to 50° C under high vacuum (ca. 10^{-6} mmHg) for 24 h in 4% (wt) yield. Bis(allyl)disiloxane 15 was also isolated from the mixture and confirmed by GC/MS and NMR (see above for spectral data). In another experiment, 23 was slowly heated to 210 °C in an evacuated flask. At 150 °C cyclic compound 24 sublimed onto the upper wall of the flask and hexamethyldisiloxane (confirmed by GC) was collected via an attached trap. Upon cooling,to room temperature, the oligomer/cyclic mixture solidified. The crystals of 24 were washed with ethanol and vacuum dried, m.p. = 208 °C (lit. 208 °C).[257] It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.39 (s, 12 H), 7.0 (s, 4 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.08, 132.15 (aromatic CH), 138.71 (ipso). HRMS (CI): M/Z, 416.1485, Calcd for $C_{20}H_{32}O_2Si_4$, 416.1480. The structure of 24 was confirmed by X-ray crystallography.

Synthesis of Poly-α,ω-4-pentenyl(1,1,3,3-tetramethyldisiloxapentylene) (25). The oligomer, 25, was prepared simultaneously by the method described above for monomer 19 in 63 % conversion. Telechelomer 25 was dissolved in hexane and chromatographed over silica gel then filtered under Ar through celite. The solvent was removed in vacuo and the oligomer was dried under high vacuum for 12 h giving the pure β isomer as a colorless oil. M_n = 960 (DP = 3.4 on average) by quantitative ^{13}C NMR end group analysis. GPC M_n = 550 (M_w/M_n = 1.3) vs. polybutadiene standards, M_n = 920 (M_w/M_n = 1.2) vs. poly(dimethylsiloxane) (PDMS) standards. GPC data using PDMS standards were obtained in $CHCl_3$ with an RI detector, complements of the analytical services division of Rhone-Poulenc Centre de Recherches, St. Fons, France. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.04 (s, 12 H), 0.52 (m, 4 H), 1.41 (m, 4 H), 2.06 (m, 4 H), 4.98 (m, 4 H, $=CH_2$), 5.80 (m, 2 H, -CH=). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.38, 17.95, 22.83, 37.43, 114.40, 139.00. ^{13}C NMR attached

proton test (APT) revealed no methyl or methine signals corresponding to the α–isomer. ^{29}Si NMR (40 MHz, $CDCl_3$): δ 6.95, 7.12, 7.29, 8.61(oligomeric homologues). IR: ν 3090 (m, vinyl), 1643 (m, allyl Si), 1255 (s, sh, SiMe), 1060 (s, br, SiOSi) 845, 800 cm^{-1}. Anal. Calcd (x = 3.4 by quantitative ^{13}C NMR end group analysis) for $C_{44.7}H_{107.0}O_{4.4}Si_{8.8}$ (found): C, 55.79 (55.89); H, 11.13 (11.01).

General Procedure for Carbosiloxadiene Polymerizations. The following general procedure was used to prepare polymers 18, 20, and 26 (see spectral data section below for the preparation of polymer 22). Monomers (ca. 1-3 g, 500-800 eq.) were vacuum transferred or added under a dry, inert atmosphere to a previously evacuated and flame dried, high vacuum valve equipped flask. The catalyst, $[(CF_3)_2CH_3CO]_2(NAr)Mo{=}CHC(CH_3)_2Ph$ (1c) (Figure 4.1), was then added (10 mg, 1 eq.) directly, without solvent, under an inert atmosphere. The homogeneous, tan colored mixtures were stirred at room temperature, and in most cases an immediate evolution of ethylene occurred accompanied by an increase in viscosity within 20 min. In some instances, the evolution of ethylene ceased and an additional aliquot (10 mg) of 1c was added to reinitiate polymerization. The reactions were then evacuated, and ethylene evolution persisted with stirring in the bulk at room temperature until viscosity reached a point as to hinder stirring. At this time the polymerizations were heated to 50-55 °C, and stirring resumed under full vacuum until magnetic agitation was no longer possible. Polymerizations were terminated by exposure to the atmosphere, and the oily polymer reaction mixtures were dissolved in chloroform or THF and analyzed by NMR and GPC. Pure polymer samples were obtained by filtering over neutral alumina in methylene chloride yielding transparent viscous oils. Reaction times ranged from

24 - 48 h, and conversions were essentially quantitative if negligible monomer was lost during evacuation. The polymers had the following spectral properties.

Poly(1,1,3,3,5,5-hexamethyltrisiloxa-2-butenylene) (18). Polymer 18 was isolated as a transparant viscous oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.40 (s), 0.93 (s), 1.49 (m), 5.24 (m, *trans*), 5.33 (m, *cis*). ^{13}C NMR (50 MHz, $CDCl_3$): δ -0.19, 1.24, 19.98 (*cis* allylic), 24.42 (*trans* allylic) 122.78 (*cis*), 124.12 (*trans*). ^{29}Si NMR (40 MHz, $CDCl_3$): δ -20.95, 4.63, 4.94. IR: ν 3010 (m), 1634 (m, allyl Si), 1260 (s, sh, SiMe), 1060 (s, br, SiOSi) 825, 800 cm^{-1}. Anal. Calcd for $C_{10}H_{24}O_2Si_3$ (found): C, 46.09 (45.91); H, 9.30 (9.32).

Thermolysis of Polymer 18. Polymer 18 (~0.2 g) was heated under N_2, or vacuum, slowly to 500 °C. The volatiles were collected by bubbling the hot vapors through CCl_4 and analyzed by GC/MS. Among the products, cyclic siloxane 29 (detailed below) was identified. GC/MS Calcd for $C_{10}H_{24}O_2Si_3$ (260 g/mol), m/z = 260, with major fragments 245, 191, and 73 a.m.u.

Poly(1,1,3,3-tetramethyldisiloxa-4-octenylene) (20). Polymer 20 was isolated as a transparant viscous oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.04 (s, 12 H), 0.50 (m, 4 H), 1.35 (m, 4 H), 1.99 (m, 4 H), 5.37 (m, 2 H,). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.41, 18.02 (Si-CH_2), 18.23 (C-CH_2-C, *cis*), 23.51 (C-CH_2-C, *trans*), 30.94 (*cis* allylic), 36.31 (*trans* allylic), 129.93 (*cis*), 130.49 (*trans*). ^{29}Si NMR (40 MHz, $CDCl_3$): δ 7.17. IR: ν 3010 (m, shoulder), 1650 (w, allyl Si), 1255 (s, sh, SiMe), 1060 (s, br, SiOSi) 845, 800 cm^{-1}. Anal. Calcd for $C_{12}H_{26}OSi_2$ (found): C, 59.42 (58.88); H, 10.83 (10.68).

Poly(1,1,3,3-tetramethyldisiloxa-*p*-phenylene-1,1,3,3-tetramethyl-disiloxa-2-butenylene), (22). Monomer 21 was dissolved in a minimum amount of dry deolefinated toluene under an inert atmosphere, and catalyst 1c was added as described above. The polymerization continued under the general conditions described above with the exception that care was taken not to evacuate the mixture to the point of precipitation. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.10 (s), 0.34 (s), 1.50 (d, internal allylic), 1.59 (d, terminal allylic), 4.89 (m, terminal CH_2), 5.24 (m, *trans*), 5.34 (m, *cis*), 5.79 (m, terminal CH), 7.56 (s, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.11, 0.37, 0.97, 1.10, 1.58, 19.80 (*trans* allylic), 24.62 (*cis* allylic), 26.45 (terminal allylic), 113.52 (terminal CH_2), 122.90 (*cis*), 124.24 (*trans*), 132.30 (terminal CH), 134.23 (aromatic CH), 140.87 (ipso). ^{29}Si NMR (40 MHz, $CDCl_3$): δ -21.60, -2.40, -2.20, 1.29, 6.57, 8.61. IR: ν 3060 (s, aromatic), 1634 (m, allyl Si), 1260 (s, sh, SiMe), 1060 (s, br, SiOSi) 830, 790 cm^{-1}. Anal. Calcd (n = 2.5 by ^{1}H NMR) for $C_{65}H_{122}O_7Si_{14}$ (found): C, 55.40 (56.98); H, 8.75 (8.65).

Poly(1,1,3,3-tetramethyldisiloxapentylene-co-1,1,3,3-tetramethyl-disiloxa-4-octenylene), (26). Polymer 26 was isolated as a transparant viscous oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.03 (s, 32 H), 0.50 (m, 11 H), 1.41 (m, 16 H), 2.00 (m, 4 H), 5.37 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.41, 18.01, 18.32, 22.97, 23.49, 31.00 (*cis* allylic), 36.34 (*trans* allylic), 37.24, 130.00 (*cis*), 130.48 (*trans*). ^{29}Si NMR (40 MHz, $CDCl_3$): δ 7.10, 7.20. IR: ν 1650 (w, allyl Si), 1260 (s, sh, SiMe), 1060 (s, br, SiOSi) 845, 800 cm^{-1}. Anal. Calcd (x = 3.4 and n = 36 by quantitative ^{13}C NMR end group analysis) for $C_{1548}H_{3659}O_{159}Si_{319}$ (found): C, 55.01 (55.25); H, 10.94 (10.81).

Formation of 1,1,6,6-Tetramethyl-1,6-disilacyclodeca-3,8-diene (27). The pure *cis,cis* cyclic dimer 27 was isolated as a white solid by sublimation (45 °C (10^{-5} mmHg)) directly from the active reaction mixture of polymer 4 in < 1 mol% yield. It had the following spectral properties. ^{1}H NMR (200MHz, $CDCl_3$), δ 0.1 (s, 12H), 1.40 (d, 8H), 5.28 (t, 4H,); ^{13}C NMR (50 MHz, $CDCl_3$), δ -2.72, 16.02, 123.11 (*cis*); Mass spectral (EI) data for $C_{12}H_{24}Si_2$ = 224 g/mol: M/Z = 224. The NMR spectra were consistent with literature data for the tetraphenyldisila derivative.[255]

Formation of 1,1,4,4-Tetramethyl-1,4-disilacyclooct-6-ene (28). The pure *cis* cyclic byproduct 28 was isolated as a clear liquid (b.p. 45 °C, 10^{-5} mmHg) by distillation directly from the active reaction mixture of polymer 5 in < 1 mol% yield. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.00 (s, 12H), 0.62 (s, 4H), 1.48 (d, 4H, J=8Hz), 5.38 (t, 2H, J = 6Hz); ^{13}C NMR (50 MHz, $CDCl_3$), δ -3.10, 8.00, 17.3, 122.9 (*cis*); HRMS (EI): M/Z, 198.1284, Calcd for $C_{10}H_{22}Si_2$, 198.1260.

Solution Preparation of 1,1,3,3,5,5-Hexamethyltrisiloxacyclonon-7-ene (29). The active polymer 18 reaction mixture (0.1g, 570 repeat unit eq.) was diluted with benzene-d_6 (0.4 M) in a Rotoflow-equipped NMR tube at room temperature. After 5 min the ^{1}H NMR spectra revealed that 36 mol% of 29 (99% *cis*) had formed. See bulk preparation of 29 for spectral data, below.

Bulk Preparation of 1,1,3,3,5,5-Hexamethyltrisiloxacyclonon-7-ene (29). The active polymer 18 reaction mixture was partially stirred and heated to 50 °C under high vacuum (ca. 10^{-6} mmHg), whereupon cyclic 29 slowly distilled, immediately upon cooling an attached condenser to -78 °C. The geometric

isomers of 29 were collected at -197 °C to give 7 mol% of 29 (80% *cis*) isolated in 5 h. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.01 (s, 6 H), 0.09 (s, 12 H), 1.52 (m, 4 H, $A_2XX'A_2'$), 5.27 (m, 2 H, $A_2XX'A_2'$, *trans*), 5.41 (m, 2 H, $A_2XX'A_2'$, *cis*). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.73 (*cis* Me), 0.86 (*trans* Me), 0.95 (*cis* Me), 1.30 (*trans* Me), 20.04 (*cis* allylic), 24.07 (*trans* allylic), 122.50 (*cis*), 123.60 (*trans*). ^{29}Si NMR (40 MHz, $CDCl_3$): δ -21.60, 2.24. IR: ν 3020 (m), 1640 (allyl Si), 1260 (s, sh, SiMe), 1050 (s, br, cyclic SiOSi), 840, 800 cm^{-1}. HRMS (EI): M/Z, 260.1083 (*cis*), 260.1091 (*trans*) Calcd for $C_{10}H_{24}O_2Si_3$, 260.1084, with major fragments; 245, 191, and 73 a.m.u. Anal. Calcd for $C_{10}H_{24}O_2Si_3$ (found): C, 46.09 (46.07); H, 9.30 (9.25).

Purification and Characterization of 4,4'-Bis(*trans*-1-propenyl)biphenyl (30). Diene 30 was donated by J.M. Boncella, and A.S. Gamble, Department of Chemistry, University of Florida and was prepared by the [Pd] catalyzed coupling of 4-bromo-β-methylstyrene. Diene 30 was recrystallized from ethanol and dried under high vacuum prior to copolymerization. It had the following spectral properties: ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.91 (d, 6H), 6.33 (m, 4H), 7.31 (m, 4H, Ar), 7.56 (m, 4H, Ar). ^{13}C NMR (50 MHz, $CDCl_3$): δ 18.55, 125.78, 126.20, 126.86, 130.59, 136.87, 139.10. UV (10^{-5} M in THF) λ_{max} = 306 nm (ε = 50600 $cm^{-1}mol^{-1}L$).

Oligomerization of 17 with Catalyst 1b. Oligomer 18 was prepared by the addition of $[(CF_3)_2CH_3CO]_2(NAr)W{=}CHC(CH_3)_2Ph$ (catalyst 1b, 1 eq.) to neat monomer 17 (670 eq.), under N_2, with stirring for 30 min in the bulk. Upon addition, rapid evolution of ethylene occurred, and the reaction was continued under intermittent vacuum for several hours until a noticeable increase in viscosity was observed. The oligomer was found to possess a M_n = 7650 (DP ~ 30)

according to quantitative ^{13}C NMR spectroscopy. Spectral data for 18 is given above with the exception of characterized terminal groups present in the oligomer as indicated in the text of chapter 6.

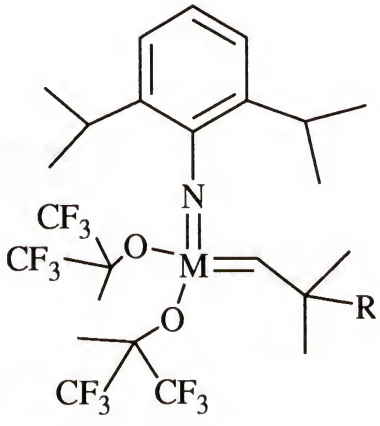
Synthesis of Poly(1,1,3,3,5,5-hexamethyl-1,1,3,3,5,5-trisiloxabutenylene-*co*-propenylenebiphenylene) (31). Copolymer 31 was prepared by the addition of biphenyldiene 30 (75 eq. vs. catalyst 1) in toluene (0.1M) at room temperature over a period of 1.5 h to the reaction mixture (containing active catalyst from 1b) of polymer 18 in 5 mL toluene. Upon dilution of polymer 18 containing active catalyst, 11 mol% hexamethyltrisiloxanon-7-ene (29) was produced immediately due to a rapid backbiting reaction. The solution was stirred for 0.5 h under N_2 and then slowly evacuated and heated over 17 h giving a viscous oil which could only be magnetically agitated at 50 °C. Bulk copolymerization was continued for several hours until stirring was no longer possible. Samples from the copolymer reaction mixture were dissolved in $CDCl_3$ and THF and analyzed by NMR and GPC, respectively. The copolymer was found to contain 16 mol% biphenylene repeat unit by ^{13}C NMR spectroscopy compared to 10 mol% of 30 added (or ~ 13 mol% vs. polymer repeat unit after subtracting % cyclics formed). Pure copolymer samples were obtained by washing with MeOH and filtering over alumina giving a light green viscous oil which resisted flow at temperatures exceeding 80° C. It had the following spectral properties: ^1H NMR (200 MHz, $CDCl_3$): d 0.087 (s), 0.15 (s), 1.49 (m, allylic 18-30), 1.75 (m, allylic 18-30), 5.24 (m, *trans* vinylic 18-18), 5.33 (m, *cis* vinylic 18-18), 6.28 (m, *trans* vinylic 18-30), 7.37(m, aromatic), 7.49(m, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): d -0.16, 1.28, 19.55, 24.43, 25.67, 122.49, 122.80, 124.05, 124.13, 125.89, 126.82, 126.88, 128.52. UV (in THF) λ_{max} = 317 nm.

CHAPTER 3

DESIGN AND SYNTHESIS OF UNSATURATED POLYCARBOSILANES

Polycarbosilanes, as introduced in Chapter 1, are polymers which contain the elements carbon and silicon within their main chain. Considerable interest has been devoted to the preparation of these polymers due to their potential application within a broad range of fields.[19] Unsaturated polycarbosilanes, also discussed previously, fall into two classes. The first consists of those polymers which alternate the unsaturation with an adjacent silicon atom (or atoms), whereas the second type constitutes those polymers which contain isolated unsaturation that is separated from the silicon functionality by saturated groups. The latter class of polymers has, for the most part, eluded preparation due to synthetic difficulties. With the exception of Weber's[104-112] anionic ring opening accounts (Figure 1.15) and other less successful and inefficient ring opening (Figure 1.14)[102] and condensation[103,174] metathesis polymerization attempts, which were detailed in Chapter 1, unsaturated polycarbosilanes of this type are rare. Although these previously explored ring opening methods find great utility throughout polymer chemistry, the requirement that strained cyclic monomers be used somewhat limits the choice of polymer structure and properties. This chapter describes the design and synthesis of novel unsaturated polycarbosilanes prepared from the acyclic diene metathesis (ADMET) condensation of carbosiladienes. It is shown herein that ADMET polymerization offers a more general selection of polymer structure when monomer structure/reactivity relationships are understood.

Throughout the remainder of this chapter, reactions involving Schrock type alkylidene metathesis catalysts, defined in Figure 3.1, will be discussed. As described in the introduction chapter, the tungsten neopentylidene catalyst, 1a, was the first well characterized tungsten alkylidene complex developed.[177] This type of alkylidene was later expanded to the more functionality tolerant molybdenum analog, shown here as the neophylidene catalyst, 1c (Figure 3.1). The preparation of the neophyl derivative was reported[195] during the development of the molybdenum based catalyst and was described at that time to be synthetically more convenient. These alkylidenes were adopted by most researchers for both the preparation of the tungsten (1b) and molybdenum (1c) analogs, and were also used in the research described here.



catalyst	M	R
1a	W	Me
1b	W	Ph
1c	Mo	Ph

Figure 3.1. Alkylidene metathesis catalysts used in ADMET polymerizations.

Carbosilane Structure and Reactivity Relationships

Efforts to understand and formulate the synthesis rules governing the metathesis condensation polymerization of acyclic dienes have resulted in specific bounds with respect to functional groups within the monomer. Previous work in ADMET research revealed some of the subtle requirements necessary for successful acyclic diene metathesis polymerization, in addition to delineating the emerging mechanistic challenges therein. As discussed in Chapter 1, Brzezinska and Wagener[247,249] used both the tungsten and molybdenum catalysts, $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)M{=}CHR$ (Figure 3.1), to derive the synthesis rules for the polymerization of ether containing dienes (Figure 1.44) while Patton and co-workers,[197,249-252] using the molybdenum catalyst, 1c (Figure 3.1), developed the requirements for carbonyl containing diene polymerizability (Figure 1.45). These researchers found, as did Schrock[185-190] in previous work, that Lewis basic functionalities are very sensitive with respect to their position in the monomer and that metathesis polycondensation is possible only if the functionality is sufficiently separated from the reactive olefin by methylene spacers. This "negative neighboring group effect" is attributed to electronic influences affecting inactive catalysis and was the first type of monomer structural restraints observed in ADMET chemistry. The second type, presented in this chapter, is steric in nature and, as will be shown, is prevalent with dienes containing alkyl substitution at the allylic position.

Konzelman *et al.*[238,239] demonstrated that the position of alkyl substituents on hydrocarbon monoenes and dienes can drastically influence olefin metathesis reactivity (Figure 1.42). Hydrocarbon dienes containing 1,1-disubstituted olefins, or substituents in the allylic position, completely rejected polymerization by ADMET chemistry when either the W (1a,b) or Mo (1c) based catalysts were

employed. As will be shown here, steric groups provide a barrier to the formation of a productive catalytic intermediate and also must be separated from the reactive olefin if successful ADMET polycondensation chemistry is to occur.

These rules for ADMET polymerization were reinforced during the initial polycarbosilane synthetic efforts described herein while using the tungstaneopentylidene (1a) or the neophylidene (1b) catalysts, $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHC(CH_3)_2R$ (Figure 3.1). The study began by attempting repeatedly, the homopolymerizations of dimethyl or diphenyldivinylsilane (2) with no success (Figure 3.2).

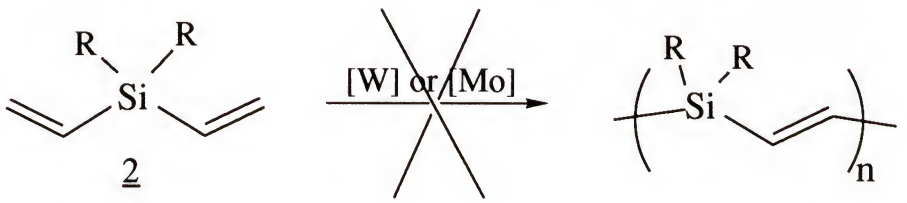


Figure 3.2 Divinylsilane resistance to ADMET, where R = Me (2) or Ph.

ADMET polycondensation of commercially available monomer 2 was predicted to give the unique alternating silaethylene polymer proposed in Figure 3.2. The polymerization attempts were performed under bulk conditions and high vacuum (10^{-6} mmHg) at varying temperatures ranging from -78 to 45 °C. A custom ADMET apparatus designed by Nel[232,235] allowed for the efficient return of refluxing monomer under these conditions and also provided for the isolation of any ethylene produced. Condensation was not observed in the case of monomer 2 and pure starting material was recovered in each case. Metathesis polycondensation using the molybdenum neophylidene (1c) catalyst was also attempted, yet like the tungsten catalyst, exhibited no metathetic activity with these α-disubstituted monomers.

The non-ADMET homopolymerizability of monomer 2 confirmed previous research of Schrock and coworkers[186,187] involving the metathesis of vinyltrimethylsilane (vinylTMS) (Figure 3.3). This work concluded that vinylTMS reacts with $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CH\text{-}t\text{-}Bu$ (1a) to form the non-catalytic metathesis products, neohexene, and the trimethylsila substituted alkylidene. This silaalkylidene, in the presence of excess vinyltrimethylsilane gave the isolable bis(trimethylsilyl)tungstacyclobutane adduct in equilibrium with the less favored (K_{eq} = 1.4×10^{-3} M at 24 °C in toluene) trimethylsilaalkylidene. According to Schrock,[187] the productive metathesis products, bis(trimethylsila)ethylene and ethylene, were not formed, and the analogous result using divinylsilane (2) above (Figure 3.2) confirmed these observations.

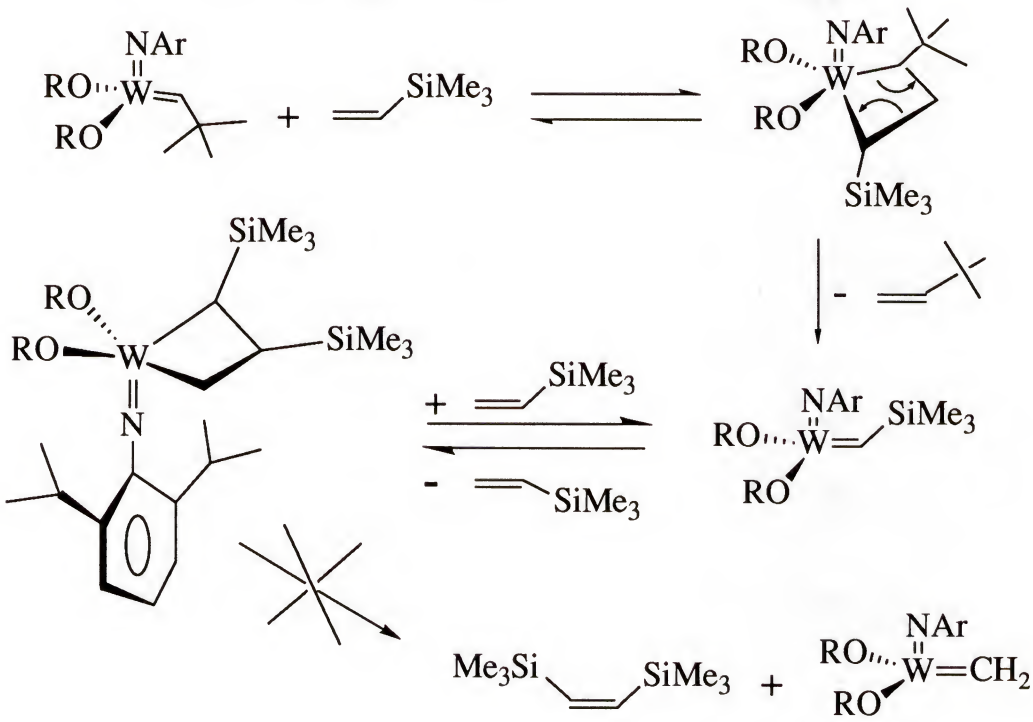


Figure 3.3. Schrock's VinylTMS Study ($R{=}CMe(CF_3)_2$).

Possible reasons for why the productive metathesis product is not formed include electronic considerations such as, π-bonding orbital overlap stabilization via the 3*d* orbitals on Si or perhaps an induced polarization of the silaalkylidene producing a stabilized silyl α-anion (discussed in chapter 1, Figure 1.1) and a tungsten cation. However, the most likely reason arises from the obvious steric interaction between the α,β-trimethylsilyl (TMS) substituents on the tungstacyclobutane ring whereby the C_α-C_β bond is weakened. An X-ray crystal structure of this tungstacycle indicates that the ring is significantly distorted due to steric repulsion between the TMS groups and the imido ligand placing the TMS groups at almost pseudoequatorial positions.[187]

These researchers also observed that when $[CF_3(CH_3)_2CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)W=CH-*t*-Bu (containing less electron withdrawing alkoxide ligands than 1a) was used, the K_{eq} for the breakup of the metallacycle was "approximately two orders of magnitude larger," and is consistent with the trend of less stable metallacycles formed from $OCMe_2CF_3$ complexes.[187] This observation may support an electronic argument for the nonproductive breakup of the metallacycle since the less electron withdrawing power of the alkoxy ligands should have a greater effect on a more polarized alkylidene intermediate. In any case, the exact reasons for why vinylTMS does not productively homometathesize were not pursued by these researchers. As will be shown later, the inability to homocondense vinyl silanes does not necessarily reflect limitations since well defined differences in monomer reactivity toward acyclic diene metathesis (ADMET) polymerization can provide an unique opportunity for polymer structural design.

These results directed the research described here to a successful strategy of separating the preventative functional group or a sterically hindering methyl group from the metal center with carbon atom spacers.[197,248] Upon doing this, it was

found that the diallylsilane monomers exhibit no resistance to productive metathesis when catalyzed by the tungsten catalyst, 1a or 1b, and afford polymers 4, 6, and 8 cleanly at low temperatures (Figure 3.4).

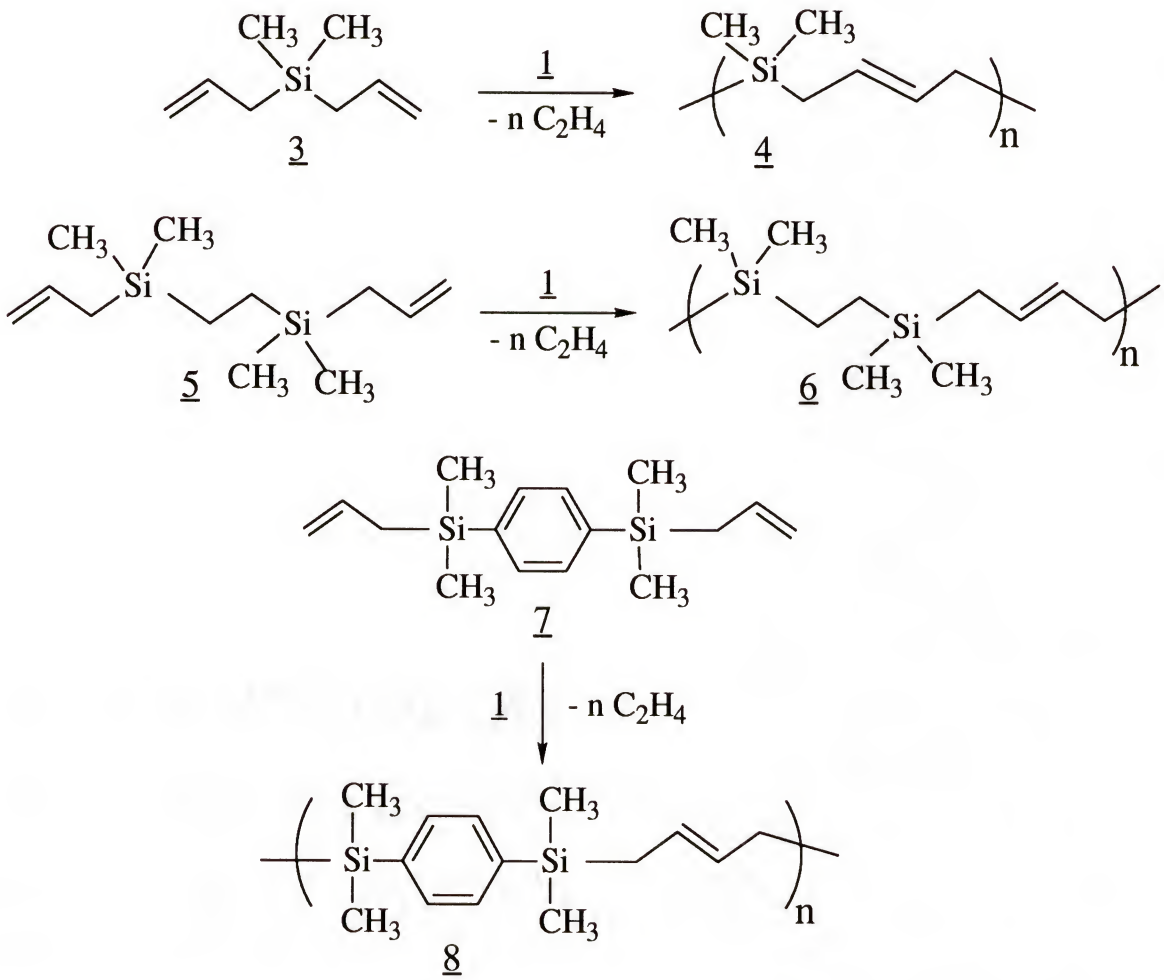


Figure 3.4. Polycarbo(dimethyl)silanes produced by acyclic diene metathesis (ADMET) polymerization of bis(allyl)carbosilanes.

The polymerization of commercially available diallyldimethylsilane (3) has been attempted previously using Re based classical metathesis catalysts, as discussed in chapter 1 (Figure 1.28).[161] This early attempt resulted in predominantly the ring closed silacyclopentene condensation product with some oligomerization, and illustrates the great dependence which catalyst choice

dictates. No formation of dimethylsilacyclopentene is observed when using catalyst 1a to polymerize monomer 3 in the bulk. However, very recently, other researchers have found that monomer 3 condenses ethylene in solution to give an equilibrium mixture of linear oligomers and the ring closed product, dimethylsilacyclopentene, when using the molybdenum catalyst 1c, and will be discussed in chapter 5.[255]

Polymer 4, possessing a different average geometric configuration, has been previously synthesized by Weber and coworkers[104-112] from the anionic ring opening polymerization of dimethylsilacyclopentene (Figure 1.15). Prior to this work, Satori[102] (Figure 1.14) reported the ring-opening metathesis polymerization of this monomer yielding low molecular weight oligomers of 4.

Bisallyl-monomers 5 and 7 were designed to expand the utility of ADMET polymerization and demonstrate that unique polymer structures can be prepared which are unattainable by other known techniques. Polymer 6 could possibly be prepared from the ring opening metathesis polymerization (ROMP) of the corresponding disilacylcooctene yet, unlike cyclooctene, this compound is not a ROMP monomer at room temperature (discussed in chapter 5). This cyclic silaalkene should possess less ring stain than cyclooctene since the Si-C bond is 0.35 Å longer than the C-C bond (Table 1.2),[28,29] and further, the presence of ring substituents typically makes ΔG more positive for ring opening processes.[205] Polymer 8 would be even less likely a result of ROMP since this method would probably require the tetrasiladibenzene dimer of 7. In any case, the synthesis of these proposed ROMP monomers would be less than trivial.

The versatility of ADMET condensation polymerization is perhaps best exemplified by the fact that dimethyldivinylsilane (2) undergoes specific cross metathesis with 1,9-decadiene (9) to give copolymer 10 (Figure 3.5). Random ADMET cross condensation copolymerization has been successful with other

systems,[236] as described previously, yet monomer specific ADMET copolymerization provides an example of how subtle reactivity requirements, which might otherwise have been construed as limits, can be productively exploited. Polymers 4, 6, and 8, as well as copolymer 10, are discussed separately in the following sections.

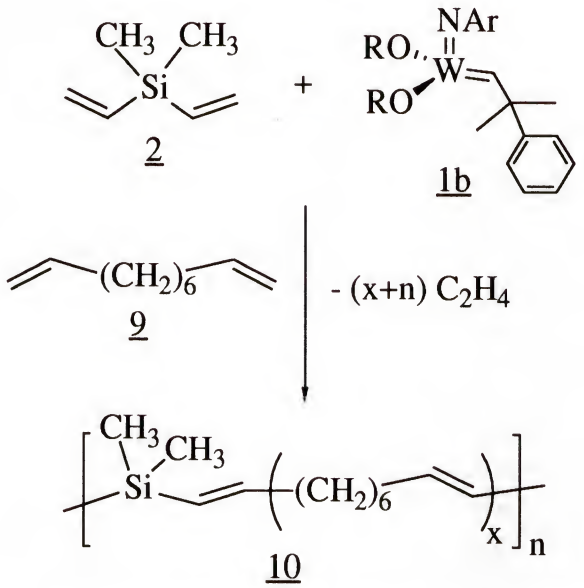


Figure 3.5. Monomer specific ADMET copolymerization.

Carbosiladiene Monomer Synthesis

The synthesis of monomer 5 was accomplished in good yield (82 % isolated pure) using the successful Grignard chemistry associated with carbosilanes.[13,14,28,258] Although various substituted monoallylsilanes are known, the diallyl monomers 5 and 7 have not been reported in the literature (Figure 3.6). The synthesis of 7 was accomplished by the "in-situ" Grignard reaction of aryl and silyl halides. Magnesium powder was used rather than magnesium turnings to accelerate the reaction since previous reports indicated both long reaction times (20-50 h) for just monosilylated benzenes and poor yields

for disilylated pyridine analogs.[259] Also, tetrahydrofuran was used as solvent rather than the more common, but very toxic, hexamethylphosphorus triamide (HMPT). The extended reaction time in the presence of activated magnesium powder, and the method of addition may have compensated for the decrease in solvent assistance from, and the lowered reflux temperature of HMPT. A reasonable yield was obtained using this technique giving an isolated 37 % of pure 7 (Figure 3.6). The product, monomer 7, was surprisingly stable and withstood heating to 100 °C on a sodium mirror during purification.

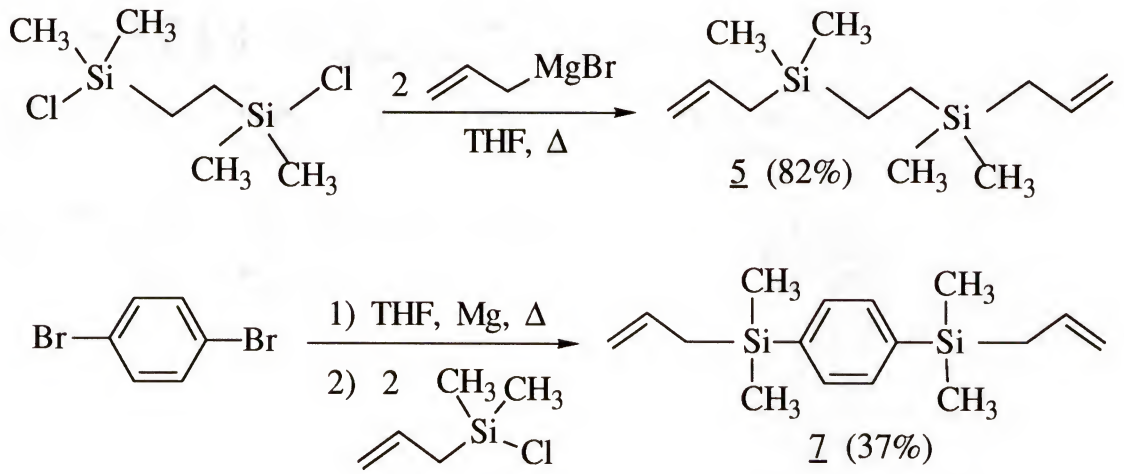


Figure 3.6. Synthesis of carbo(dimethyl)siladienes 5 and 7.

ADMET Polymerization of Carbosiladienes

As distinguished from ROMP chemistry, acyclic diene metathesis (ADMET) polymerization is an equilibrium step propagation condensation type polymerization, where the production and removal of ethylene (when using terminal olefins) drives the reaction. As previously described,[231-240,245-252] and reviewed in chapter 1 (Figure 1.39), ADMET polymerizations are performed in the absence of solvent under step (bulk) conditions, high vacuum, and with a typical monomer to catalyst ratio of 500-1000:1. In most cases, immediate

evolution of ethylene is observed at room temperature along with an obvious increase in viscosity within a short time (ca. 30 min). The polymer chemistry is very clean with no side products being evident except pure ethylene condensate and trace amounts of cyclic products when formation of the cyclics is favorable. Polymers 4 and 6 do form trace amounts of the 10- and 8-membered cyclic carbosilaalkenes, respectively, and will be discussed in chapter 5. Physical characterization and thermal analysis results for the unsaturated polycarbosilanes are compiled in Table 3.1 which also contains physical data for copolymer 10.

Table 3.1. Polycarbo(dimethyl)silanes prepared via ADMET polymerization.

Polymer	M_n[a] (GPC)	M_n[b] (NMR)	M_w/M_n[c]	% Trans[b] (NMR)	T_g (°C)	TGA[d] N_2(Air)
4	12000	-	1.94	81	-67	330
6	50000	-	1.10	73	-59	440(230)
8	1500	1300	1.34	47	-46	-
10	7800	6400	2.10	75[f]	g	-

[a] Relative to polystyrene standards. [b]Calculated from quantitative ^{13}C NMR (see experimental). [c]After washing with methanol. [d]Temperature (°C) at which 10% weight loss occurs. [f]Octenamer units. [g]T_m = 43 °C, T_c = 30 °C (Figure 3.14).

Relative number average molecular weights (M_n) were determined in THF by gel permeation chromatography (GPC) relative to polystyrene standards. Exact number average molecular weights were calculated from quantitative ^{13}C NMR end group analysis, when possible, by integration of the terminal vinyl carbon signals versus the internal olefin carbon signals. Polymers 8 and 10, unlike polymers 4 and 6, are low enough in molecular weight to display these visible endgroups in both their ^{1}H and ^{13}C NMR spectra, and thus they permit M_n

determination by NMR endgroup analysis (Table 3.1). The fact that ADMET polymers possess vinyl endgroups has been a convenient asset in the determination of the molecular weights for these polymers. ADMET polymers typically exhibit good correlations (below $M_n \sim 20000$) in number average molecular weights, as determined by gel permeation chromatography, end group analysis, elemental analysis, and vapor pressure osmometry.[232,235,236,252] This is unequivocal data for the presence of vinyl endgroups in ADMET polymers. Integrations from quantitative ^{13}C NMR, rather than the ^{1}H NMR, spectra were used for quantitative characterization since better resolution and sensitivities are obtained from ^{13}C NMR. This is best exemplified when considering determination of the *trans/cis* geometric isomer ratios where these resonances are frequently unresolved in the ^{1}H NMR spectra. When adequate pulse delays were employed (5 times the longest T_1, see experimental), and a gated decoupled pulse sequence is used, real number average molecular weights were obtained and are compared to relative values obtained from GPC analysis (Table 3.1).

Polymer 4 differs from the same, yet mostly *cis*, polymer reported by Weber[104] (Figure 1.15) since 4 contains an unprecedented high average *trans* content (81 %), as measured by quantitative ^{13}C NMR. This observation is typical of ADMET chemistry, and seems to be retained here for these unsaturated polycarbosilanes (Table 3.1). Polymer 6 was produced in the highest molecular weight for the polymerizations examined (GPC $M_n = 50000$) (Table 3.1). The extended reaction time and maintained catalyst activity are presumably responsible for the higher molecular weight of polymer 6 versus that of 4, 8, and copolymer 10.

The molecular weight distributions in ADMET polymers typically approach 2, as expected from step polymerizations which are statistically confined to the Carother's equation introduced in Chapter 1.[7] The narrower distributions of

polymers 6 and 8 are undoubtedly due to loss of some low molecular weight fractions during purification (Table 3.1). It is later shown, in Chapter 3, that purification is not necessary before analysis of these polymers by GPC since byproducts are not observed in the final reaction mixtures. Typical reaction mixtures of ADMET polymers exhibit monomodal molecular weight distributions of linear chains terminated with alkene end groups.

In some cases, the factor limiting the degree of polymerization for ADMET chemistry is the thermal stability of the catalyst. Schrock's tungsten catalyst (1), and the less stable[177] unsubstituted methylidene ($NAr(OR)_2W{=}CH_2$) generated during ADMET polymerizations (Figure 1.43) decompose below 65-75 °C.[232] This temperature range is below the melt temperature of many polymers, and the solid state intervenes when ADMET polymer begins to grow. A change of state retards the high conversions required for step growth polymer chemistry. However, since polycarbosilanes 4 and 6 are viscous oils at low temperature, reasonably high molecular weight polymers are obtained provided prolonged catalyst activity. Figure 3.7 displays the ^1H and ^{13}C NMR spectra for high molecular weight 73 % *trans* polymer 6.

The ^1H and ^{13}C NMR spectra of polymer 6 illustrate that the concentration of terminal vinyl carbons are below the limit of detection for NMR endgroup analysis. These spectra of the polymer's final reaction mixture also demonstrate the exceptionally clean mode of propagation common to ADMET polymerizations. No byproducts are observed in the NMR spectra of the reaction mixture and all protons and carbons within the repeat unit of polymer 6 are easily assigned due to its perfectly regular structure. The terminal vinyl protons (4.64, 5.56 ppm) and carbons (112.58, 135.15 ppm) for monomer 5, used to prepare polymer 6, are completely absent.

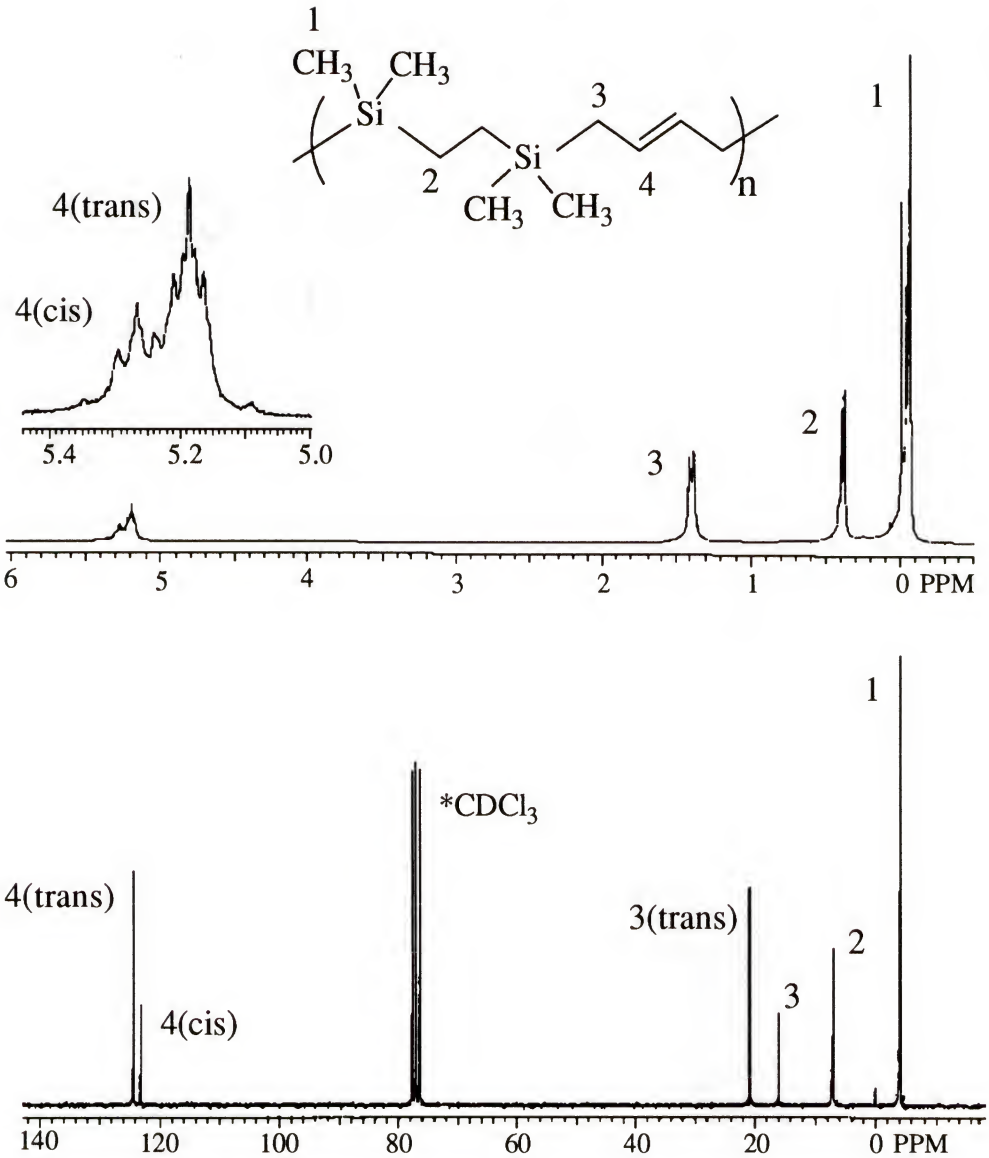


Figure 3.7. 200-MHz ^{1}H and 50-MHz ^{13}C NMR spectra of high molecular weight 73 % *trans* polymer 6 final reaction mixture.

The internal vinylic *cis* and *trans* protons are only partially resolved in the ^{1}H NMR spectra, whereas this ratio is easily determined from integration of the corresponding carbon signals in the quantitative carbon spectra (73 % *trans*). Similarly, the *cis* and *trans* allylic protons (1.41 ppm) are indistinguishable whereas the *cis* and *trans* allylic carbons (16.07 ppm and 20.87 ppm, respectively) differ by more than 4 ppm (Figure 3.7). Interestingly, the methyl substituents on

silicon are also affected by the *cis/trans* geometry in both the proton and carbon spectras despite being three atoms away from the internal olefin. Not surprising, however, is the 0.8 ppm difference observed for the *cis* and *trans* affected silicon atoms in the ^{29}Si NMR spectra (see experimental).

During ADMET polymerizations, ethylene was collected as the reaction progressed at -197 °C via an attached collection flask. This flask could be isolated from the reaction using high vacuum valves, and allowed for the return of volatile monomer after ethylene evacuation. Under these conditions, the high volatility of ethylene provided for its detection by mass spectral analysis during the polymerizations (Figure 3.8).

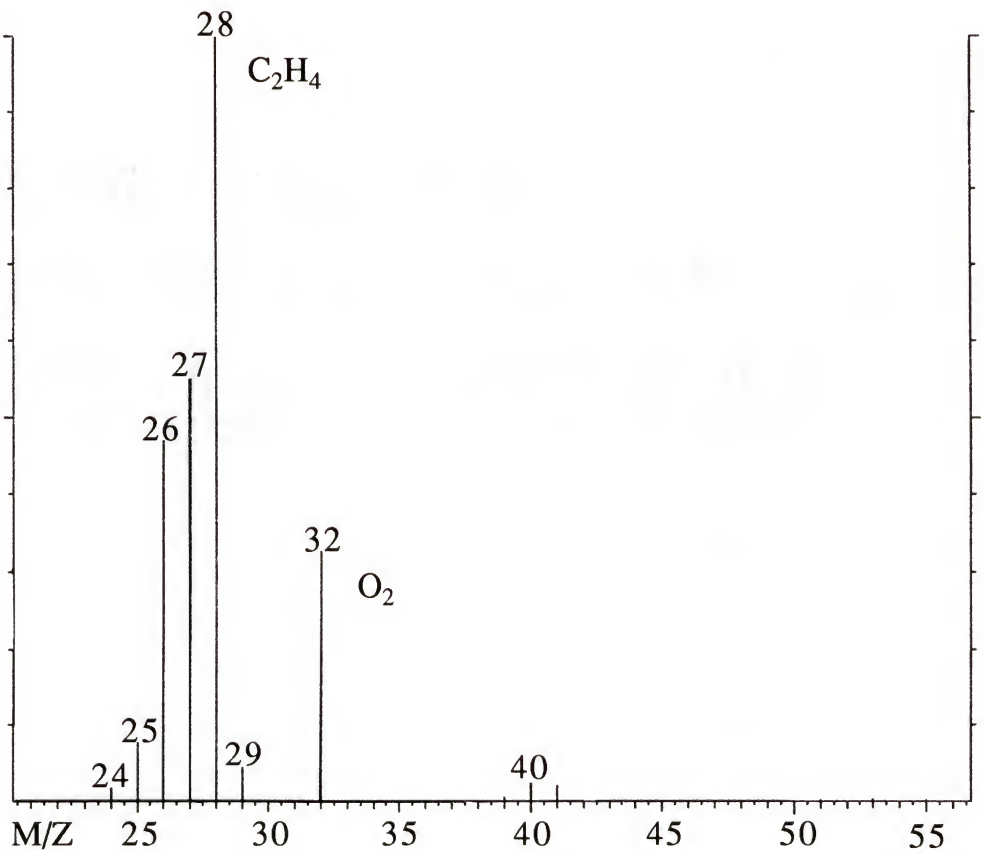


Figure 3.8. Electron impact (EI) mass spectrum of the ADMET condensation product, ethylene (C_2H_4 mol.wt. = 28 g/mol).

Figure 3.8 displays a typical electron impact (EI) gas chromatagraph mass spectrum (GC/MS) of the polymerization byproduct, ethylene. Ethylene exhibits a parent mass at 28 m/z which is followed by successive fragments decreasing by 1 to 24 m/z. These specific fragment ions were essential in order to conclude that the compound was indeed ethylene since contaminating N_2 (entering the sample during analysis), which shares the same molecular mass as ethylene, was also present.

Aromatic polymer 8 gave the lowest molecular weight for the series of unsaturated polycarbosilanes (Table 3.1). Treatment of aromatic monomer 7 with catalyst 1b resulted in the immediate evolution of ethylene yet the reaction stopped after just 30 minutes. The mixture was allowed to stir for an extended time with no further condensation, while repeated catalyst additions and purification attempts proved unsuccessful in achieving high molecular weight. Figure 3.9 compares the ^{1}H NMR spectra of the olefinic regions of monomer 7 and polymer 8.

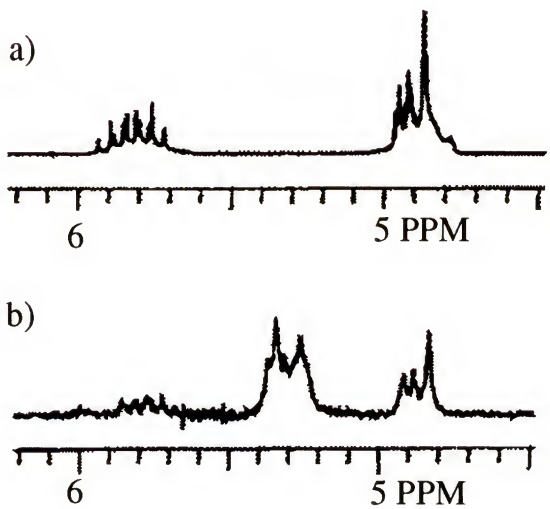


Figure 3.9. 200 MHz ^{1}H NMR spectra of the olefinic region for (a) monomer 7 and (b) polymer 8.

The formation of internal unsaturation (5.33 ppm, spectrum a) and the decreased intensities for the terminal vinyl proton signals (4.69, 5.57 ppm, spectrum b) illustrate that incomplete condensation had occured. The low molecular weight of polymer 8 and likewise the low *trans* content (47 %) most likely are due to decomposition of the catalyst by some evasive impurity. Degenerate or inter-chain trans-metathesis reactions which favor the thermodynamic *trans* isomer are secondary equilibria in ADMET chemistry which compete with productive terminal olefin condensation. This is consistent with the known higher reactivity of the tungstalkylidene (1) toward less substituted olefins.[185,187] The failure of this monomer to polymerize is particularly discouraging since its low volatility is practically ideal for the ADMET technique in that it allows for the use of continuous high vacuum at these polymerization temperatures which ensures the complete and constant removal of ethylene.

Monomer Specific ADMET Copolymerization

It is clear that dimethyldivinylsilane (2) is completely inert to productive homopolymerization by metathesis with alkylidene catalysts 1b,c, and so it came as a surprise when copolymers containing this monomer could be produced by the ADMET technique. Copolymer 10 (Figure 3.5) was prepared by treating monomer 2 with catalyst 1b and heating, initially, to 40 °C and then stirring at room temperature for 111 h before an equimolar (0.05 mol) amount of 1,9-decadiene (9) was added under high vacuum. Upon addition of 9, an immediate evolution of ethylene occurred and the viscosity of the mixture increased, indicating that the catalytic species had remained active. The co-metathesis reaction was continued with intermittent evacuation for 5 days, yet the observation of ethylene ceased just several hours after the addition of monomer 9.

The plausible formation of a copolymer was based on the assumption that an equilibrium had been established between dimethyldivinylsilane (2), the silavinylalkylidene, $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHSiMe_2CH{=}CH_2$, and the disilavinyltungstacyclobutane, 11 (Figure 3.10), before the addition of 1,9-decadiene - analogous to Schrock's observations with vinyltrimethylsilane.[187] If this was the case, then the productive metathesis reaction involving 2 would have the best chance of occurring, before the presumably more favored homopolymerization of 1,9-decadiene ensued. Figure 3.10 illustrates the mechanism for the formation of copolymer 10.

As the mechanism indicates (only pertinent equilibria are shown) - similar to Schrock's mechanism (Figure 3.3) - the tungstalkylidene (1b) reacts with divinyldimethylsilane (2) and looses 3-methyl-3-phenylpentene to give the silavinylalkylidene in equilibrium with the presumably non-productive disilavinyltungstacyclobutane, 11. Upon addition of unhindered monomer 9, an additional competing equilibrium is then established producing the less hindered α,β-disubstituted tungstacyclobutane adduct now containing the substituent products of 2 and 9. This tungstacycle should possess significantly less strain than the α,β-diTMS complex or the α,β-disilavinylalkylidene, 11, and thereby allow productive cleavage giving the metathesis cross product of 2 and 9, and the very reactive tungstamethylidene. At this point, alkylidene competition for the unhindered diene should be faster versus the hindered divinyldimethylsilane (2) resulting in a copolymer with a low percentage of random, yet isolated, dimethyldivinylsilane linkages.

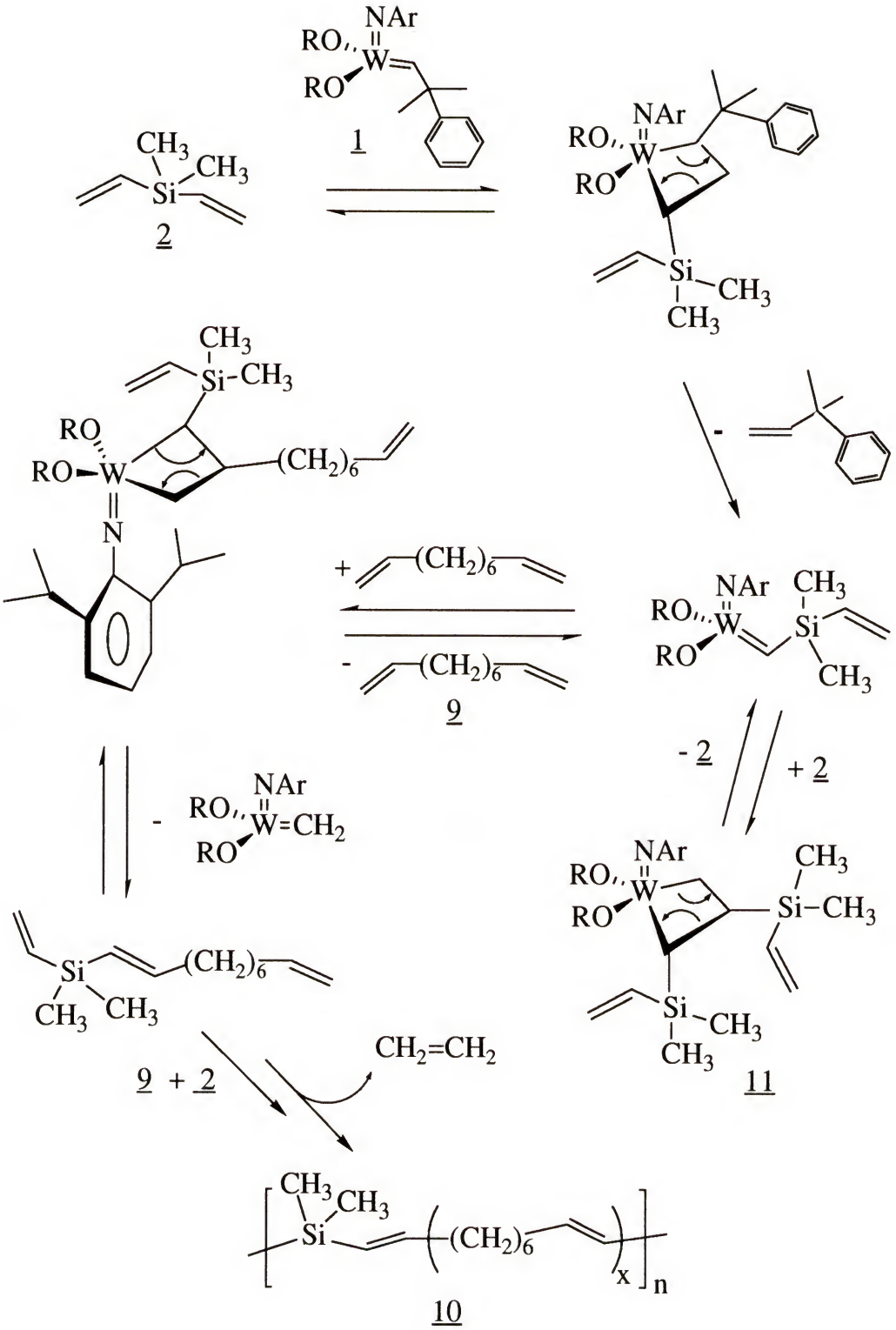


Figure 3.10. Monomer specific copolymerization of dimethyldivinylsilane (2) and 1,9-decadiene (9) (R = $CMe(CF_3)_2$).

An NMR scale reaction of monomer 2 and catalyst 1b in benzene-d_6 (see experimental) was also performed with the hope of identifying the intermediates proposed in Figure 3.10. A low excess mixture of 2 and 1b (28:1) was analyzed immediately by ^{1}H and ^{13}C NMR and indicated that the disilasubstituted metallacycle, $(RO)_2(ArN)W[CH(SiMe_2CH{=}CH_2)CH(SiMe_2CH{=}CH_2)CH_2]$ (11), and free 3-methyl-3-phenylpentene were produced. Table 3.2 gives a comparison of the ^{1}H and ^{13}C NMR data for the observed metallacycle, 11, and Schrock's similar disilasubstituted complex obtained from reaction of vinylTMS and catalyst 1a (Figure 3.3).[187] Only the tungstacyclobutane ring carbons and protons are compared in Table 3.2. The designations, α and β refer to the metallacycle protons and carbons α and β to the tungsten atom, where α' refers to the unsubstituted position in the metallacycle on which there are two non-equivalent protons.

Table 3.2. Chemical Shifts for Silasubstituted Tungstacylobutane Complexes.

Tungstacyclobutanes	Hα	Hβ	Cα	Cβ
$W[CH(SiMe_3)CH(SiMe_3)CH_2]$-$(NAr)(OR)_2$	5.66(α') 4.36(α')[a] 4.04	-0.77	110.8(α') 105.7	5.2
$W[CH(SiMe_2Vi)CH(SiMe_2Vi)$-$CH_2](NAr)(OR)_2$ (11)	NR[b] 4.51(α')[a] 4.12	-0.60	110.8(α') 104.3	4.6

[a]dd, J = 5 and 9 (for both complexes). [b]Not resolved due to excess 2. For complete NMR assignments for 11, see experimental in chapter 2.

Good agreement is found for the corresponding chemical shifts for these two similar compounds. It is clear that the vinylsilane substituent on the

metallacyclobutane ring influences the chemical shifts of the ring protons and carbons vs. those for the diTMS-substituted metallacycle. This is most clearly observed for the C_α signals which are idential (110.8 ppm) for both compounds and does not contain the affective substituent. Most of the remaining proton and carbon signals representative of the two molecules (not represented in Table 3.2) are less than 0.1 ppm different. For example the methyl group on the alkoxy ligands of the diTMStungstacyclobutane complex gives the two different signals, ^{1}H: 1.56, 1.76 ppm and ^{13}C: 18.1, 18.9 ppm, whereas the disilavinyl complex (11) exhibits signals for this group at, ^{1}H: 1.66, 1.81 ppm, and ^{13}C: 18.3, 19.0 ppm, respectively. The largest difference between the chemical shifts for the two tungstacyclobutanes are found with the H_β and C_β signals and are consistent with the large range of shifts these atoms typically exhibit since they seem to be most severly affected by subtle geometric fluctuations, as well as polarizations.[177,187]

An equilibrium between the disilavinyltungstacycle (11) and 2, analogous to that reported for vinylTMS (Figure 3.3), was not observed by ^{1}H or ^{13}C NMR at 200 MHz and 50 MHz, respectively. Schrock[187] has shown that the tungstacycle is much preferred over the alkylidene for the diTMS case, yet a measurable equilibrium does exist (K_{eq} = 5.3 x10^{-3} at 41 °C). For the presumed equilibrium of 11 and the silavinylalkylidene - as expected at these concentrations - alkylidene proton resonances were not observed in the range typically measured for such species (e.g., 10.11 ppm for W=C*H*SiMe$_3$),[187] and the spectrum remained unchanged for 24 h at 40 °C.

Upon addition of a slight excess of 1,9-decadiene to the solution, again no immediate change in the principal resonances was evident. However, after 48 h at 42 °C, ethylene was observed (5.33 ppm for =C*H*) and new resonances indicative of internal vinylic octenylene protons (5.52 ppm) and carbons (130.7, *trans* and 130.2, *cis*) appeared. Resonances corresponding to internal vinylsilane carbons

were also evident to a small extent (see experimental). At this point, the fate of the metallacycle is unclear due to severe broadening and complexities in the spectrum which remained unchanged shortly after reaction was observed with 1,9-decadiene (9).

Experiments were also designed to test the effect of the exposed vinyl functionality within metallacycle 11 (Figure 3.10). Additional stability of the tungstacyclobutane possessing substituents bearing α-vinyl groups (11) may be invoked from coordination of the tethered olefin into the electrophilic metal center. Nucleophilic coordination of functional groups contained within a metallacycle substituent is known to occur for Lewis basic groups such as esters[189] and amines,[199] and have also been suggested for olefins.[206] 1,4-pentadiene was used as a control to test the influence of the vinyl substituent on catalysts 1b and 1c, without the influence of the steric barrier caused by the methyl groups on silicon (Figure 3.11).

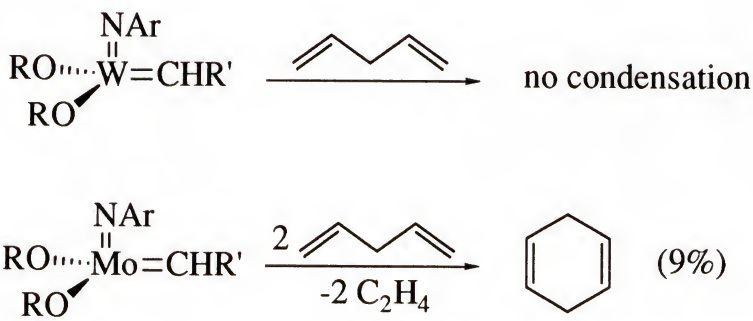


Figure 3.11. Reactions of 1,4-pentadiene and catalysts 1b and 1c.

Tungsten catalyst 1b was treated with excess 1,4-pentadiene in the bulk and in solution, yet condensation of ethylene was not observed for any case after repeated attempts. Only pure starting material was detected by NMR. The reaction of molybdenum catalyst 1c, under the same conditions, did condense ethylene to produce the expected 6-membered ring, in solution or in the bulk.

Although no evidence exists for the tungsten/olefin complex suggested in Figure 3.11, the known stability of tungstacycles and the possibility for coordination in this system may provide some explanation as to its failed reactivity toward the self condensation of 1,4-pentadiene and the sluggish co-metathesis of dimethyldivinylsilane (2). The less electrophilic molybdenum catalyst, on the other hand, is known to form less stable metallacyclobutanes and therefore may suggest why this catalyst does metathesize 1,4-pentadiene. The low conversions, however, could indicate the presence of an impurity and warrants additional purification and a confirmation of these results before substantial conclusions could be derived.

While dimethyldivinylsilane does copolymerize with 1,9-decadiene (9), albeit to a low percent of the polymer and with obvious less reactivity than 1,9-decadiene, there is no evidence of consecutive vinylsilane linkages. The vinylsilane repeat units are isolated. The 50 MHz ^{13}C NMR spectra of copolymer 10 is displayed in Figure 3.12. The spectrum illustrates that both vinylsilane end groups (signals 7 and 9) and octenylene end groups (signals 6 and 10) are present in the copolymer which implies that complete cross metathesis had not occurred with the unsubstituted monomer 9. Pure monomers 2 and 9 were also retrieved from the reaction mixture indicating that unhindered diene 9 failed to polymerize to maximum conversions.

These results provide evidence for the loss of catalytic activity before a cross metathesis equilibrium was established. If the copolymer had been completely terminated with vinylsilane end groups in addition to the complete consumption of unhindered decadiene monomer 9, then additional information could be extracted concerning alkylidene discrimination of such monomers when allowed to reach equilibrium. Nevertheless, the fact that dimethyldivinylsilane copolymerizes with an unsubstituted monomer demonstrates that nonproductive cleavage of the

bis(dimethylvinylsila)tungstacyclobutane (11) is caused by steric factors rather than orbital overlap stabilization or other electronic considerations dominant in the proposed intermediate silaalkylidene, $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHSiMe_2CH{=}CH_2$ (Figure 3.10).

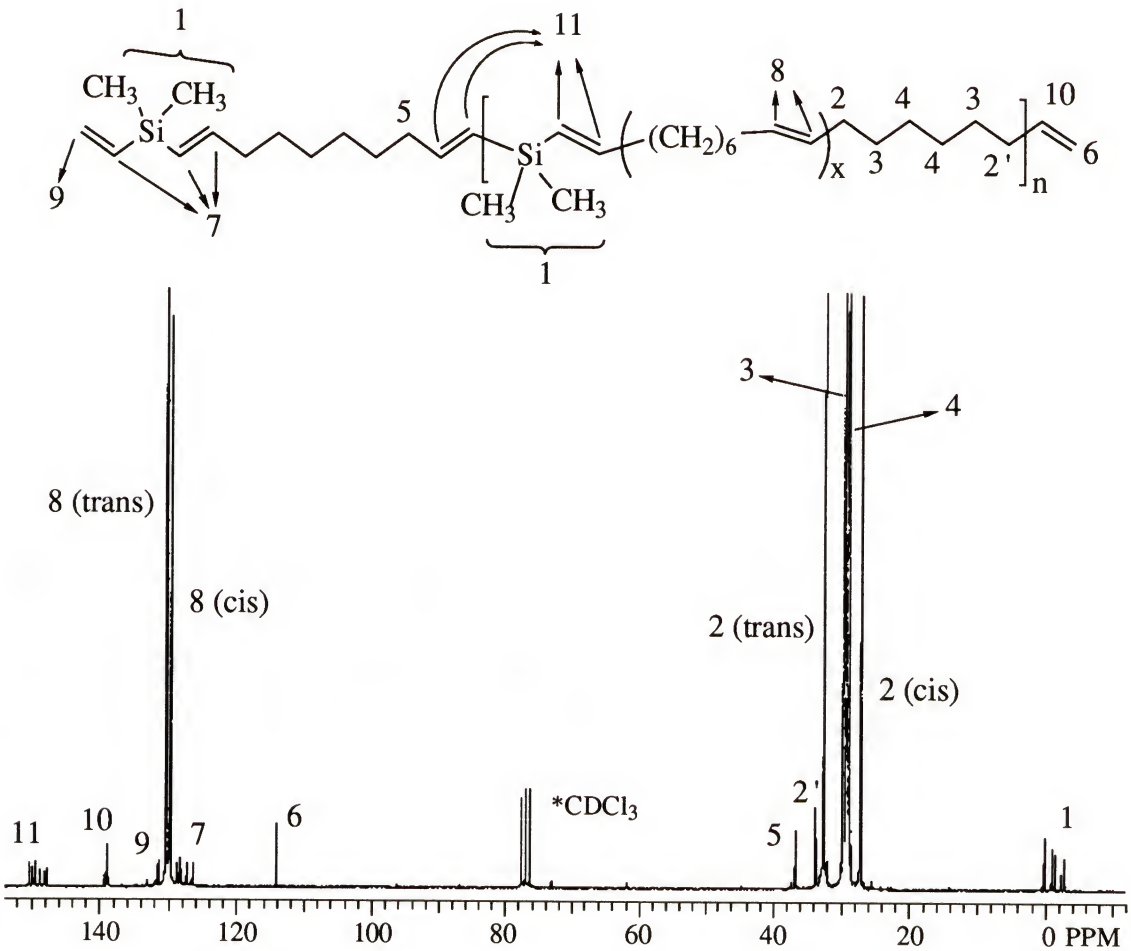


Figure 3.12. Quantitative 50 MHz ^{13}C NMR spectra for copolymer 10.

The nonequivalent carbon signals of copolymer 10 are labeled in Figure 3.12. The spectrum exhibits the 75 % average *trans* geometric content found for the octenylene internal olefinic carbons (signal 8) as well as the typical large difference (>5 ppm) in the *cis* and *trans* octenylene internal allylic carbons (signal 2). Terminal allylic (signal 2') and vinylic (signals 6 and 10) octenylene carbons

are also resolved. Signal 5 is assigned to the allylic vinyl silane carbon based on the down field shifts representative of the vinylic carbons of vinyl silane (signals 11). The assigned terminal vinylic carbons of vinylsilane (signals 7 and 9) were determined by ^{13}C NMR attached proton test (APT) technique, which distinguishes between methyl, methylene and methine carbons. The internal vinylic carbons on vinylsilane (signals 11) are represented by six distinct signals which are essentially of equal abundance by integration. These six signals are reasonably assigned as geometric isomers of the two internal vinylic groups within the divinylsilane linkage. Each nonequivalent carbon in one vinyl group is affected by the geometry of the other, α-vinyl group. Therefore for the two chemically nonequivalent vinyl carbons within the divinylsilane linkage there exists three affective geometries; *cis/cis*, *cis/trans*, and *trans/trans*. Similarly, the methyl groups on silicon (signals 1) are also influenced by the vinylsilane geometries giving three signals for each of the isomers listed above and two signals arising from the two possible configurations of the terminal vinylsilane group. The terminal vinylsilane carbon signals are more complex since the symmetry exhibited by the internal vinylsilanes is lost. Eight signals (6 methine and 2 terminal methylene olefinic carbons) in all are expected for this group yet not all are resolved due to the octenylene internal olefin carbon signals found in the same region. Similarly, the vinylic and allylic vinyl silane protons are not resolved in the ^{1}H NMR spectrum of copolymer 10 due to the broad resonances found for the methylene, allylic, and vinylic octenylene protons. The Si-Me protons are present, however, as five sharp singlets (0.04 - 0.28 ppm) attributed to the three isomers of the internal divinylsilane linkage and to the two terminal isomers, as expected.

Figure 3.13 displays the FTIR spectra of a) poly(octenylene) homopolymer prepared by the ADMET condensation of 1,9-decadiene[235] and b) copolymer 10.

Poly(octenylene) exhibits two characteristic bands in the IR which quantitatively represent the *cis* and *trans* olefins. As indicated in Figure 3.13a, the methylene groups in poly(octenylene) give the strong band at 1470 cm^{-1} whereas the alkene gives the shoulder at 1404 cm^{-1} due to in-plane bending of the *cis* isomer, and the strong band at 970 cm^{-1} characteristic of the out-of-plane distortion of the *trans* isomer. These olefinic bands have been used previously to estimate the geometric isomer ratio in this polymer.[260] The C=C stretching absorbtions (~1620-1650 cm^{-1}) are generally too weak in poly(octenylene) to be observed and do not allow quantitation due to the polarity enhanced absorbtion of the *cis* isomer.[261]

The FTIR spectrum of copolymer 10 (Figure 3.13b), although more intense, illustrates two fundamental differences. While the octenylene linkages are represented by those characteristic bands found in spectrum (a) (1470 cm^{-1} and 970 cm^{-1}), new bands appear which unequivocally identify the vinylmethylsilane linkage. Vinylsilanes display a characteristic absorbtion at 1600 cm^{-1} and 1410 cm^{-1} which are both present in spectrum (b).[262] Although the 1410 cm^{-1} band is contained within the methylene absorbtion of the octenylene methylenes, the vinylsilane band at 1600 cm^{-1} along with accompanying shoulders (representing various isomers) is resolved completely. Further, the strong, sharp absorbtion at 1260 cm^{-1} due to the Si-Me stretch is a classic fingerprint of this group and in copolymer 10, no exception is found.[262]

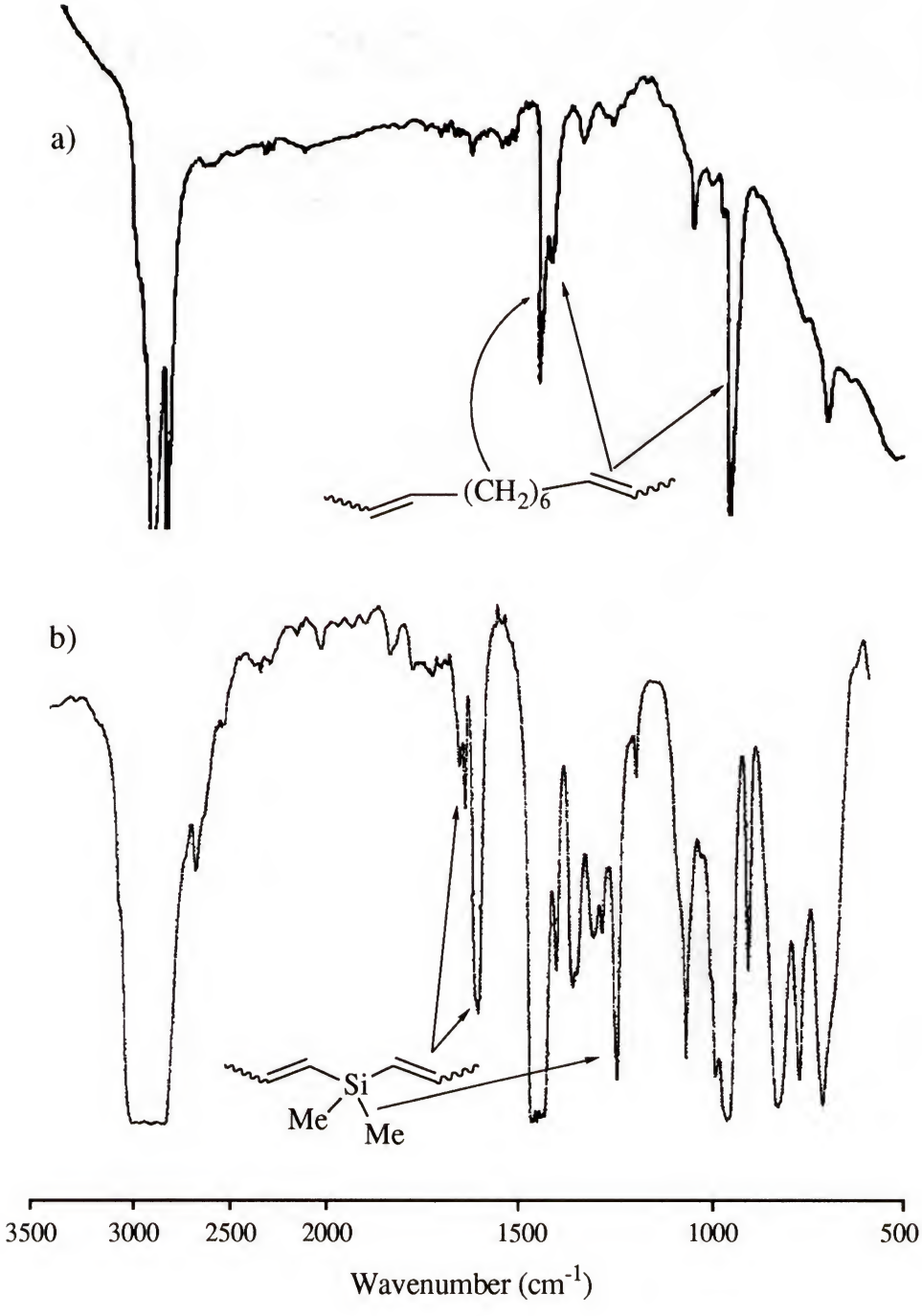


Figure 3.13. IR spectra of a) poly(octenylene) homopolymer and b) copolymer 10.

Polycarbosilane Thermal Properties

Silicon containing polymers are especially valuable materials due in part to their extreme use temperature range.[18,19,38] Polysiloxanes, or silicones, detailed in chapter 1, are particularly important for low and high temperature applications and are more appropriately compared in the following chapter. Due to the relatively few examples of polycarbosilanes known, however, their thermal behavior for the most part, is unknown. Physically, the polymers studied here are best described as being transparent viscous liquids at room temperature, even at high molecular weights. This behavior is expected for polymers containing substituted silicon atoms within the repeat unit due to the discontinuity in size and bonding character along the chain which discourages interchain packing and subsequent crystallization. These effects enable the polymer chains to remain mobile at very low temperatures and therefore they should exhibit low glass transition temperatures (T_g).

Thermal properties for the unsaturated polycarbosilanes were determined by two techniques. Glass transition (T_g) temperatures were measured by differential scanning calorimetry (DSC) and thermal stability was determined by thermal gravimetric analysis (TGA). The glass transition temperatures, reported in Table 3.1, for polymers 4, 6, and 8 were reproducible (to within 2 °C) and essentially independent of heating rate. Thermal data for 81 % *trans* poly(dimethylsilabutenylene) (4, Table 3.1) concur with literature values reported by Weber[104] for the same polymer possessing a high *cis* stereo chemistry. Weber reported a T_g = -64 °C for this polymer, whereas 81 % *trans* polymer 4 was found to possess a T_g = -67 °C, an essentially identical value despite the differences in *trans* content. Figure 3.14 displays the DSC thermograms for polymer 6 and copolymer 10. The thermogram of polymer 6 exhibits a T_g = -59 °C, and is

representative of the unsaturated carbosilane homopolymers which all display glass transition endotherms upon heating. Melting transitions were not observed for the high *trans* content homopolymers whereas the previously reported high *cis*[104] (Weber reports pure *cis* geometry) analog to polymer 4 apparently exhibits a melting transition at 25 °C. Predictably, the stereoregularity of the high *cis* polymer enhances interchain order which induces varying degrees of crystallinity.

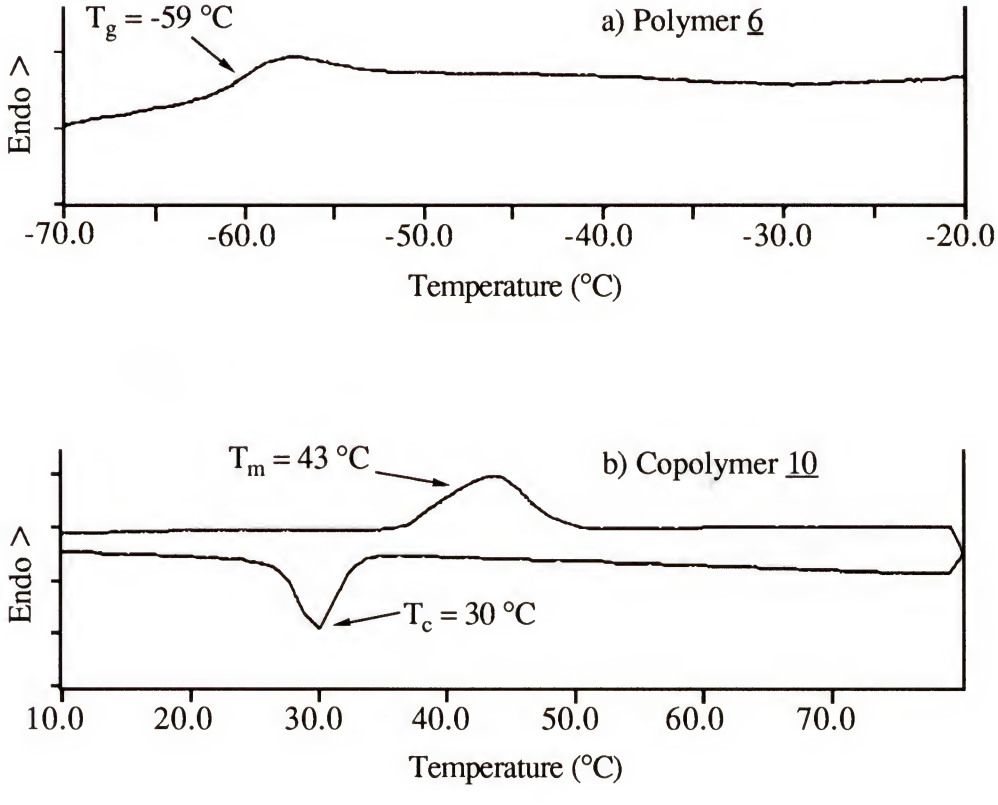


Figure 3.14. Differential scanning calorimetry (DSC) thermogram of a) polymer 6 at (10 °C/min) and b) copolymer 10 (10 °C/min).

A glass transition above -100 °C was not observed for the less flexible copolymer 10. However, reproducible melting and crystallization transitions were observed as expected since copolymer 10 can be viewed as a slightly modified poly(octenylene) which is known to exhibit a melting and recrystallization transition dependent upon the average geometry.[232,235] The

dimethyldivinylsilane linkages comprise only 6 % of the total number of polymer repeat units on average in copolymer 10 where the octenylene homo-linkages are 75 % average *trans* geometry. The DSC behavior of a sample of 77 % *trans* poly(octenylene)[232] produced by the ADMET homopolymerization of 1,9-decadiene (9) is used here for comparison. The effect of introducing divinylsilane units into the backbone of poly(octenylene) decreases the melting temperature of the homopolymer, from 52 °C, for 77 % *trans* poly(octenylene), to 43 °C for 75 % *trans* copolymer 10 (Figure 3.14). Recrystallization occurs upon cooling at essentially the same temperature as that of the homopolymer; 30 °C vs. 32 °C respectively. Although this comparison is qualitatively instructive, certain inaccuracies may exist. While, the melting point of poly(octenylene) has been shown to be linear with percent *trans* content despite great differences in sample molecular weight,[232] copolymer 10 is but an oligomer and may deviate significantly from this trend. Nevertheless, the fact that the kinetics of recrystallization for the two are very similar lends some credibility to the melting point lowering effect of divinyldimethylsilane.

The thermal gravimetric analysis in nitrogen for high molecular weight polymer 6 is depicted in Figure 3.15. Good thermal stability for polymer 6 is observed where essentially zero percent weight is lost upon heating from 50 - 400 °C. Rapid weight loss begins just above 400 °C, and the sample is completely volatilized at 480 °C under nitrogen. This rapid and complete elimination of mass is indicative of the structural purity exhibited by these regular polymers. ADMET polymerizations are strictly confined to one repeat unit forming mechanism thereby prohibiting structural irregularities such as branching or cross linking. The fact that these polymers completely decompose thermally in a linear fashion over a narrow temperature range of 50 °C (5 minutes) implies that only one mechanism of decomposition is responsible. Steps in the TGA curve are frequently observed

for unsaturated silicon polymers due to thermal cross linking where formation of a three dimensional network enhances thermal stability.[108,110] Decomposition mechanism singularity, in this case, is good evidence for the existence of pure polymer structures.

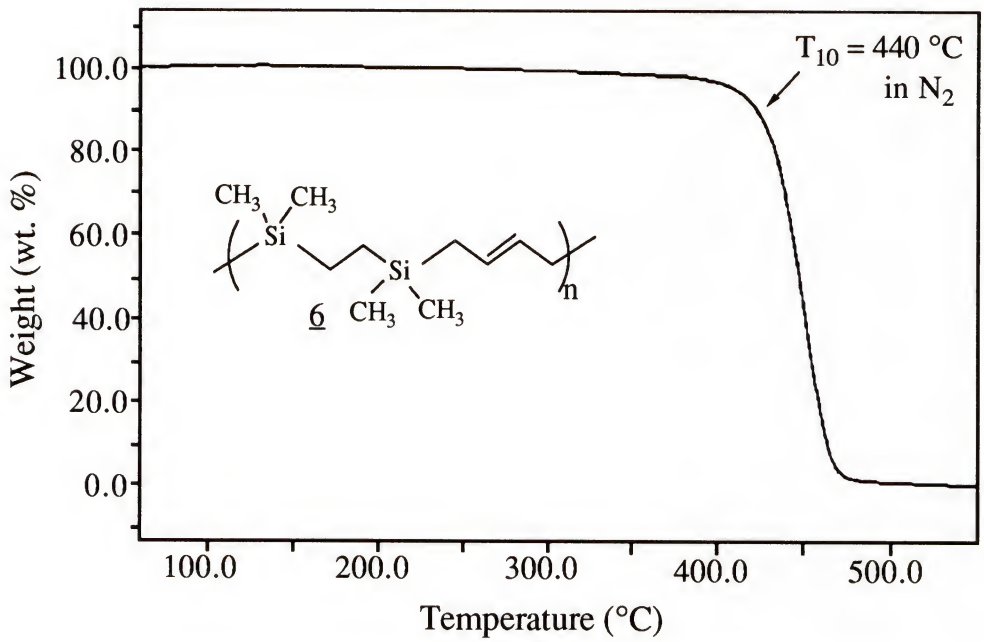


Figure 3.15. Thermal gravimetric analysis (TGA) for polymer 6 at 10 °C/min.

Polymer 6 decomposes as expected much earlier in air, where rapid weight loss begins at 230 °C. Decomposition is slower in air, reaching a maximum of 90 % weight loss at 550 °C. A black residue (most likely silicon oxide/carbide) representing 10 % of the sample, remains after heating to 700 °C.

Conclusions

Acyclic diene metathesis (ADMET) polymerization offers a new route to poly[carbo(dimethyl)silanes]. The use of highly active, Lewis acid free Schrock tungsten alkylidene catalysts facilitates a clean polymerization path, affording new

unsaturated silicon containing polymers with known vinyl end groups. The predominantly *trans* and high molecular weight polycarbosilanes produced exhibit low glass transition temperatures and good thermal stability in nitrogen. Divinyldimethylsilane does not homopolymerize via ADMET polymerization yet does undergo specific copolymerization with 1,9-decadiene where the vinylsilane linkages are isolated. This result supports a steric argument for why the vinylsilanes do not homocondense by metathesis using these catalysts.

CHAPTER 4

DESIGN AND SYNTHESIS OF UNSATURATED POLYCARBOSILOXANES

As discussed in Chapter 1, organofunctional siloxane polymers (Figure 1.3) are important macromolecules due to their unique combination of properties including, an extreme use temperature range, hydrophobicity, biocompatibility, and gas permeability.[11,19,20,30] These valuable characteristics have prompted an interest in the design of new hybrid systems where siloxane incorporation into an organic based polymer is used to tailor specific properties.[34-36] For the most part, past efforts have focused on block copolymers of poly(dimethylsiloxane) with a variety of polyolefins, polycarbonates, and polyoxyalkylenes which, for example, find application as polymer blend compatibilizers.[37]

Polycarbosiloxanes as a specific class of siloxane based polymers possess alternating carbon and siloxane linkages within the main chain and are of considerable interest to silicone chemists. Although the performance of carbon based polymers simply do not compare to silicones, when considering the applications for which silicones are used, e.g., oils, elastomers, plastics, etc., regular organic based substitutions within a siloxane polymer provide one primary advantage - carbon is much less expensive than silicon. The conversion of natural silicates (or sand) to pure elemental silicon then to organohalosilanes via the Rochow process[31,32] (Figure 1.2), then to cyclosiloxane monomers, and finally to polymer can not compete today, in cost, with the ease in which abundant organic monomers are obtained directly from petroleum. It is proposed that by

incorporating carbon into the siloxane backbone of a silicone polymer, mechanical property sacrifices could be minimized and thermal stability even improved, while lowering overall material cost.

The synthesis of these polycarbosiloxane systems currently is confined to the polysilarylene-siloxanes,[38,43-47] typically prepared by the condensation of dichlorosilanes and disilanolbenzenes (Figure 1.4), and to a limited number of saturated polycarbosiloxanes prepared by the ring opening polymerization of cyclocarbosiloxanes (Figure 1.5).[46-48] These techniques exhibit obvious limitations. Silanol/halosilane polycondensation is accompanied by various redistribution and cyclization reactions, whereas the ring opening of cyclocarbosiloxanes requires the synthesis of strained cyclic monomers which confines polymer structure and thus properties. This chapter presents an alternate method for the preparation of polycarbosiloxanes and in addition provides for unique olefin functionality regularly placed within the main chain.

Wherein Chapter 3 described the design and synthesis of unsaturated polycarbosilanes via the acyclic diene metathesis (ADMET) polymerization of carbosiladienes using the Lewis acid free metathesis catalyst, $[(CF_3)_2CH_3CO]_2(NAr)W{=}CHC(CH_3)_2R$ (1a,b, Figure 3.1), ADMET chemistry is applied here to the polymerization of dienes containing the important siloxane functionality. Monomer structural requirements for the successful ADMET polymerization of methyl-substituted carbosiloxadienes using the molybdenum alkylidene catalyst, $[(CF_3)_2CH_3CO]_2(NAr)Mo{=}CHC(CH_3)_2Ph$ (1c, Figure 3.1), are presented and rationalized based on the current understanding of this chemistry. The polymers presented here, as well as, main chain unsaturated polycarbosiloxanes in general, were not known previously.

Carobosiloxadiene Structure and Reactivity Relationships

As discussed in Chapter 1, ADMET polymerizations are possible only if vinyl addition reactions are eliminated.[231-240,246-252] This singularity of reaction type is accomplished when Lewis acid-free metathesis catalysts such as, $[(CF_3)_2CH_3CO]_2(NAr)M{=}CHC(CH_3)_2Ph$ (Figure 3.1) are employed, where M = Mo (1c) or W (1a,b), and Ar = 2,6-C_6H_3-*i*-Pr_2. The molybdenum alkylidene (1c, Figure 4.1) has been shown to be more tolerant to polar functionality[185,195,223] than is the tungsten analog and was initially chosen here for the polymerization of these oxygen containing monomers. However, as will be shown in Chapter 6, the tungsten catalyst (1b, Figure 3.1) also exhibits no intolerance with the siloxane functionality.

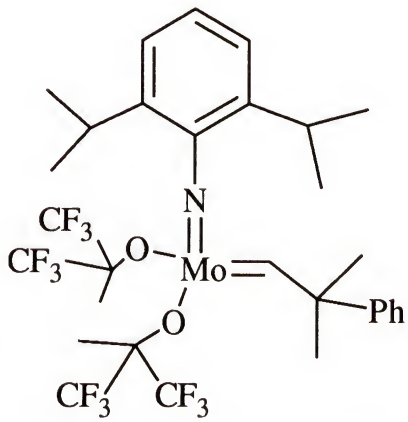


Figure 4.1. Lewis acid free alkylidene catalyst (1c).

Catalyst 1c has been used, very recently, to synthesize cyclic ethers,[198] amines,[199] and lactams[199] from dienes, and has also demonstrated the ability to initiate the living cyclopolymerization of dipropargyl esters.[97] ADMET polymerization offers a complementary use for these catalysts, and it has been shown that when particular synthetic "rules" are obeyed, this chemistry is also

compatible with many functionalities of importance to polymer chemistry.[197,246-252]

As described in Chapter 3, acyclic diene monomers containing Lewis basic functional groups exhibit a "negative neighboring group effect" which is attributed to electronic influences affecting inactive catalysis unless the functionality is sufficiently separated from the reactive olefin by methylene spacers.[246-252] It was also shown that monomer steric restraints were observed in ADMET chemistry and that these groups provided a barrier to the formation of a productive catalytic intermediate and also must be separated from the reactive olefin if successful ADMET condensation polymerization is to occur. Divinyldimethylsilane does not homopolymerize in the presence of catalyst 1 yet will specifically copolymerize with an unhindered diene monomer producing a copolymer where the divinylsilane linkages are isolated.

The possibility that a less crowded Si-O environment (vs. that of Si-CHR) would permit productive homometathesis of vinyl silicon monomers prompted the attempted polymerization of divinyltetramethyldisiloxane (Figure 4.2). Recent work by Marciniec and co-workers[170-174] (detailed in chapter 1, Figures 1.29 and 1.30) demonstrated that monovinyl silanes containing alkoxy substituents underwent successful metathesis condensation, in less than quantitative conversions, when catalyzed by $RuCl_3(H_2O)_n$ or $RuCl_2(PPh_3)_3$. These results ensured access to functionalized silicon containing small molecules by metathesis yet are not amenable to the strict confines dictated by step polymerization kinetics. Ru based catalysts of this type constitute a form of the classical metathesis derivatives discussed in chapter 1, and despite their nonconformity to acyclic olefins, they have been shown to be excellent catalysts for the ring opening polymerization of strained cycloalkenes.[218,219]

The simplest divinylsiloxane monomer was tested first. Commercially available divinyltetramethyldisiloxane (Figure 4.2) was found to be completely resistant to productive metathesis when treated with either the molybdenum catalyst, 1c, or the tungsten analog. Pure starting material was recovered, upon repeated attempts, in each case.

Figure 4.2. Bis(vinyl)tetramethyldisiloxane fails to polymerize via ADMET.

For the tungsten catalyzed case, the most likely cause for productive metathesis inhibition is that the α-dimethyl substitution in 14 sufficiently prevents productive cleavage of the required α,β-disubstituted metallacycle due to steric restraints, as found with divinyldimethylsilane in chapter 3. The reason for metathesis failure using the molybdenum catalyst 1c is less clear, however, and arises presumably from the previously reported[194] instability of molybdacycles (vs. tungstacyclobutanes) formed from the reaction with vinyl silanes such as, CH_2=CHSiMe_3, and not due to electronic interferences attributed to the β-oxygen. In fact, other β-oxo monomers such as diallylethers,[198,249] as well as the even more basic diallylamines,[199] have been shown to undergo homometathesis with catalyst 1c and is sound evidence for this presumption. Furthermore, the Lewis basicity of the siloxane oxygen is less than that of an ether due to 2*p*-3*d* delocalization of oxygen's loan pair of electrons and would not be as aggressive in offering such a "negative neighboring group" electronic effect.

In an attempt to confront, once again, the dimethyl "steric effect" demonstrated in chapter 3 with dimethyldivinylsilane (2), an α-monosubstituted monomer was designed, while retaining the siloxane functionality. A

divinyldisiloxane monomer (containing Si-H bonds) was envisioned where one methyl group on each silicon atom in bis(vinyl)tetramethyldisiloxane (Figure 4.2) was replaced with a hydrogen atom. Schrock and co-workers[194] have demonstrated that the neopentylidene derivative of catalyst 1c reacts at low temperature (-30 °C) with vinyltrimethylsilane to form the silaalkylidene and the disilamolybdacycle, yet this metallacycle was considerably less stable than the tungsten analog. As with the tungsten system described in chapter 3, the productive metathesis product, bis(trimethylsila)ethylene, was not observed. From these results and those described in chapter 3, it was reasoned that the combination of reduced steric interaction by substitution of the methyl groups with hydrogen in bis(vinyl)tetramethyldisiloxane (Figure 4.2), and low temperatures, might result in successful productive metathesis.

This new silane functionality presented problems, in itself, since the Si-H bond is, in many instances, very reactive. Silanes (Si-H) can be viewed as hydridic species since the polarization of the Si-H bond is opposite that of C-H due to the extreme electropositivity of Si, as discussed in chapter 1. Furthermore, many organometallic complexes activate the Si-H bond toward the hydrosilation[74] of olefins, and the reactivity of this functionality has not been previously demonstrated with Scrock type alkylidenes.

If hydrosilation chemistry is excluded as a predominant reaction for the Si-H bond in the presence of catalysts such as, 1c and the tungsten analog 1b, then, for the most part, the silane functionality can be considered to be hydridic only when the silicon atom is sufficiently attacked by a good nucleophile. Therefore, since the neophylidene catalyst, 1c, is not a good source of nucleophiles which would promote the displacement, the opportunity to condense, via metathesis, a silane containing olefin seemed reasonable. Simple model studies designed to test the

tolerance of the silane group, as well as the extreme of electrophilic silicon functionalities, the Si-Cl group, were carried out as shown in Figure 4.3.

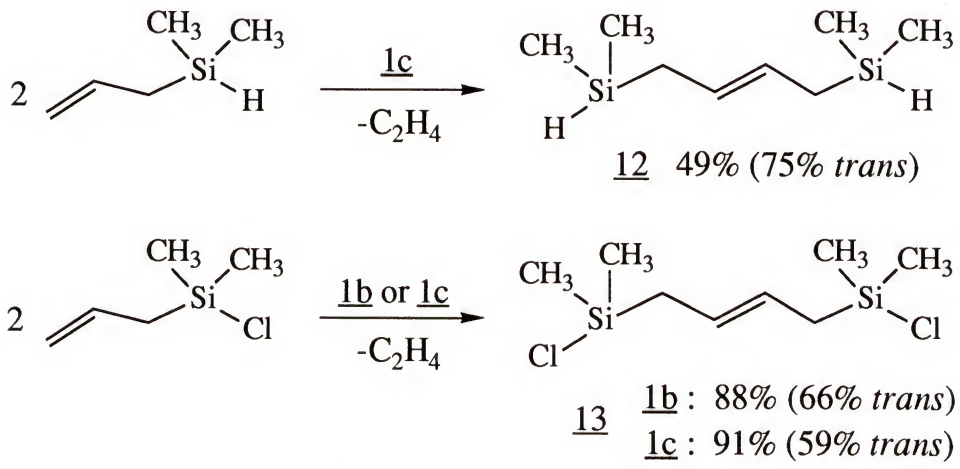


Figure 4.3. ADMET of reactive silicon functionalities.

The molybdenum neophylidene catalyst 1c condensed excess allyldimethylsilane to bis(dimethylsilyl)-2-butene (12) in 49 % conversion. Although the yield of the reaction was low, the experiment did illustrate at least some tolerance of the molybdenum catalyst to the silane functionality. Allylchlorosilane, on the other hand, seems to be tolerated even better by both the tungsten and molybdenum neophylidenes 1b, and 1c, respectively (Figure 4.3). Bis(chlorodimethylsilyl)-2-butene (13) was produced in much higher conversions than dimer 12, where it appears that the homolytically strong Si-Cl bond prevails in the presence of these catalysts and the reactivity of the various potential nucleophiles (i.e., alkoxy, imido, and alkylidene ligands) are not sufficiently nucleophilic.

With the tolerance of catalyst 1c to the Si-H bond established, the divinylsiloxane monomer, bis(vinyl)dimethyldisiloxane (14), mentioned above was synthesized. The hydride displacement, with lithium aluminum hydride (LAH), of the corresponding dichlorosiloxane (Figure 4.4) gave a moderate

isolated yield of 14. Vinylsilanes are especially reactive compounds[74] and extreme care was taken to avoid contact with air and moisture. Figure 4.4 illustrates the synthetic scheme for the synthesis of 14 and its reaction with molybdenum catalyst 1c.

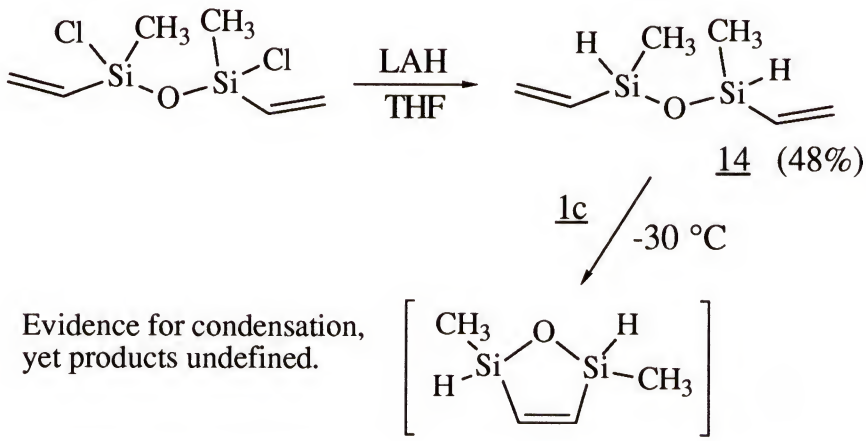


Figure 4.4. Synthesis of 14 and reaction with catalyst 1c.

Bis(vinyl)dimethyldisiloxane, 14, was vacuum transfered on to catalyst 1c at liquid N_2 temperature and allowed to warm slowly to -30 °C. The products of the reaction were not clearly defined, yet an indication that metathesis condensation had occurred was evident. Upon examination of the product mixture by ^{1}H NMR, new resonances indicative of internal vinylic protons were found, as well as a substantial downfield shift of the Si-*H* signal (4.72 ppm for 14 vs. 5.10 ppm for the product). The 5-membered cyclic condensation product, proposed in Figure 4.4, is a likely candidate since dihydrofuran has been produced, by Brezinska and Wagener,[249] from the metathesis condensation of diallylether using catalyst (1c). The large shift in the Si-*H* resonance is also best explained by a cyclic structure. The ^{13}C NMR spectrum of the product mixture, in addition to starting material signals (135.6 and 136.7 ppm, =*C*H$_2$ and =*C*H-, respectively), also exhibits a signal at 128.0 ppm, which best corresponds to an internal vinylic carbon, as

determined by attached proton test (APT). The exatct identity of the products was unclear and changed with time upon exposure to air, presumably due to decomposition.

These somewhat inconclusive results directed this research to the successful strategy of separating the preventative functional group or sterically hindering methyl group from the olefin with methylene spacers. In fact, one methylene spacer is sufficient, such that neat bis(allyl)tetramethyldisiloxane (15) (Figure 4.5) metathesizes readily upon catalytic treatment with catalyst 1c giving, exclusively, the seven-membered cyclic product, 16, in essentially quantitative conversion. Evolution of ethylene was observed below 0° C and was complete within 40 minutes as the reaction mixture was allowed to warm to room temperature.

This rapid and exclusive cyclization, in the absence of solvent, indicates that the diallyl compound 16 prefers to adopt the conformation predicted by the *gem*-dimethyl, or Thorpe-Ingold effect[264-265] - placing the olefins in close proximity and/or stabilizing the transition state to ring closure. Recent solvent free, and quantitative, metathesis mediated cyclizations of carbonyl containing dienes have been reported by Patton[252] by using the *gem*-dimethyl effect and catalyst 1c. Earlier attempts to produce cyclic alkenes via olefin metathesis were restricted to solution techniques and were seldom quantitative,[198,199,266-270] with few exceptions.[271,272] Cyclic compound 16 has been prepared previously by Weyenberg *et al.*,[256] from the hydrolytic condensation of 1,4-bis(dimethylmethoxysilyl)-2-butene. The compound's refractive index and boiling point were reported.

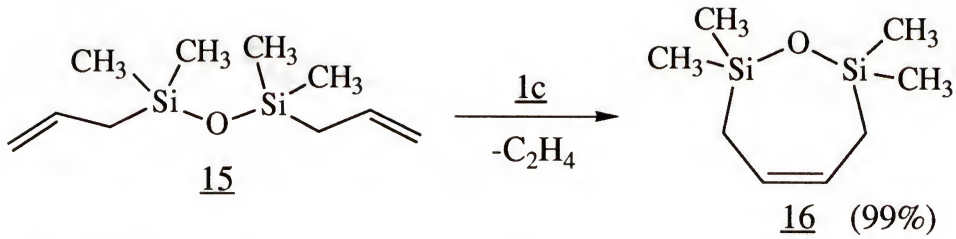


Figure 4.5. Exculsive metathesis cyclization condensation of bis(allyl)disiloxane.

Figure 4.6 displays the 200 MHz ^{1}H NMR spectrum of cyclosiloxalkene 16. The allylic protons of 16 (1.53 ppm) do not differ significantly from the allylic signals in diene 15; however, the ring structure does influence the ^{29}Si resonance greatly, as expected. Carbosiloxadiene 15 exhibits a ^{29}Si resonance at 5.61 ppm, whereas the ^{29}Si signal in cyclosiloxalkene 16 is observed at 8.62 ppm. The cyclic structure is also exposed in the FT-IR spectrum, where a broad and strong absorption is observed at 1035 ν, characteristic of the cyclic Si-O-Si vibration.[262]

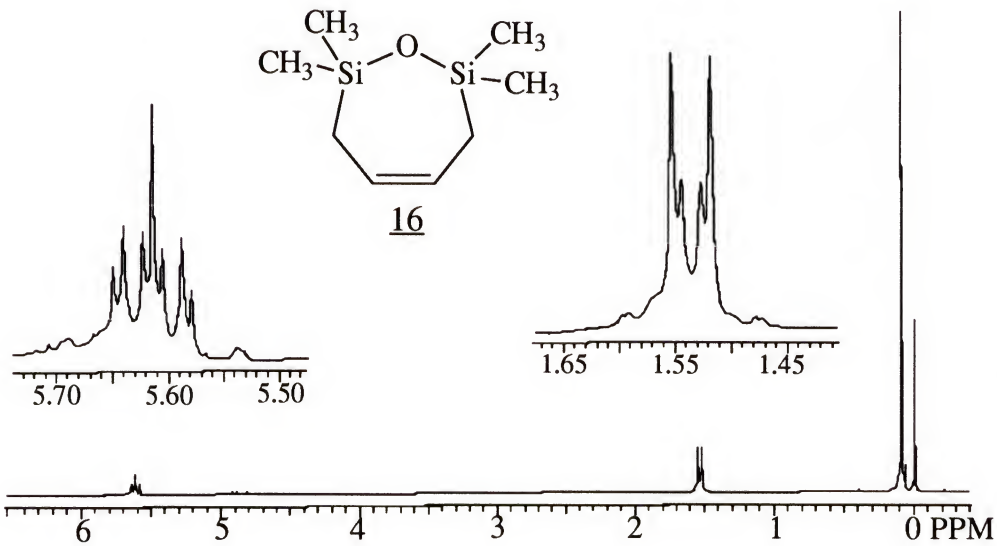


Figure 4.6. 200 MHz ^{1}H NMR spectrum of cyclosiloxalkene 16.

With the above results clear, efforts were then focused on preventing cyclization. Although the seven membered cyclodisiloxalkene (16) was favored,

even under bulk conditions, the potential ring forming reaction should be kinetically discouraged for the formation of higher membered cyclic compounds. Extended carbosiloxadienes were then designed which would prefer polymerization over cyclization. This was easily accomplished by either extending the disiloxane linkage of monomer 15, to the trisiloxane (see monomer 17) or by extending the propenyl appendage within the monomer (see monomer 19) as shown in Figure 4.7.

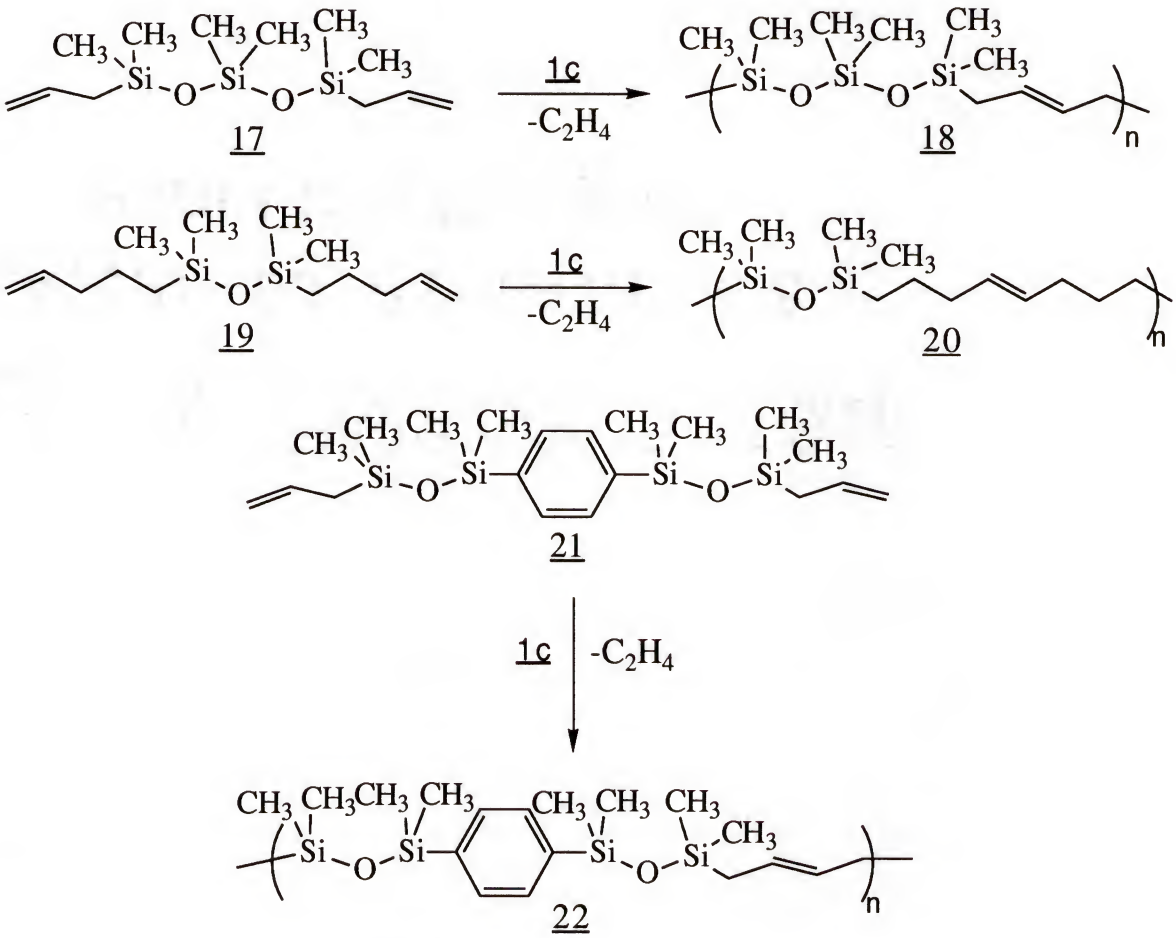


Figure 4.7 ADMET polymerization of carbosiloxadienes.

It was found that monomers 17 and 19 show no resistance to homometathesis and polymerize readily via ADMET condensation, when catalyzed by 1c, to give

polymers 18 and 20 cleanly at low temperatures. Furthermore, arylene monomer 21 (Figure 4.7) and α,ω-diene telechelomer 25 (presented in a later section, Figure 4.13) polymerize to polymers 22 and 26, respectively, and demonstrate the generality of this polymerization method as applied to the siloxane functionality.

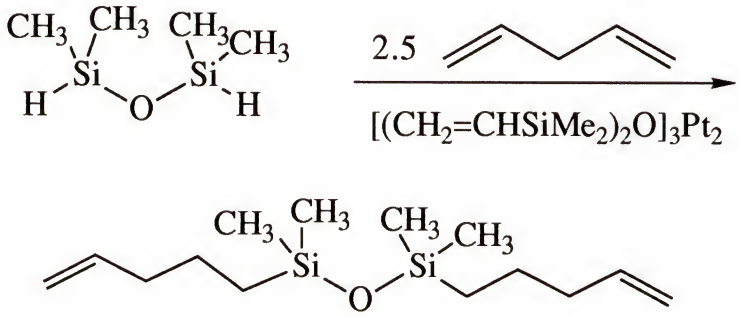
Like the polycarbosilanes detailed in chapter 3, these polymers are especially unique in that there appears to be no known method for their effective preparation. Ring opening metathesis techniques could be envisioned for the preparation of polymers 18 and 20, which would require nine and eleven membered rings, respectively, yet would be unlikely candidates due to a lack of angle or translational ring strain required for ROMP. As will be shown in chapter 5, the cyclosiloxalkene required to produce polymer 18 by ROMP is formed from a back biting reaction of polymer 18, and constitutes evidence for its non-polymerizability by ROMP.

Carbosiloxadiene Monomer Synthesis

Compounds 15 and 17 were prepared analogously to the synthesis of the diallylsilane monomers presented in chapter 3 (Figure 3.6). The reaction of allylmagnesium bromide in THF with the corresponding dichlorosiloxane gave monomers 17 and 19 in good yield under mild conditions.

The synthesis of monomer 19 (Figure 4.8) and α,ω-diene telechelomer 25 (Figure 4.13) was accomplished by the hydrosilation of neat 1,4-pentadiene with tetramethyldisiloxane catalyzed by tris(divinyltetramethyldisiloxane)$Pt_2(0)$ (Karstedt's catalyst).[254] This catalyst (shown in Figure 4.13) provided a convenient route to 19 giving the major β-adduct isomer (~95 % as detected by GC) in 17 % isolated conversion. Pure diene 19 was isolated by fractional distillation and ^{13}C NMR attached proton test (APT) spectroscopy was used to

determine that the pure β-isomer had been obtained. Methyl and methine carbon signals corresponding to the α-isomer were not detected in the ^{13}C NMR spectra at 50 MHz.



pure β-isomer 19 (17% isolated)

Figure 4.8. Hydrosilation synthesis of monomer 19.

When considering that bulk oligomerization was favored under these hydrosilation conditions to give predominantly 25, pure diene 19 was obtained in reasonably good yield (Figure 4.8). No advantages were perceived for this reaction in solution since cyclization would have undoubtedly been a significant competing reaction. Six, seven, and eight membered rings resulting from the various one to one isomeric adducts are possible and would have conceivably lowered yields due to the additional separation required. The synthesis of telechelic diene 25 by hydrosilation oligomerization using Karsted's catalyst is detailed in a later section.

Monomer 21 was prepared by the condensation of allylchlorodimethylsilane with 1,4-bis(hydroxysilyl)benzene (Figure 4.9). Pyridine was used to avoid the acid catalyzed silanol polymerization for which this reagent is typically used.[38,43-46] No oligomerization was observed, however, 4 % (wt.) of the crystalline cyclic byproduct 24 was isolated. It was determined that byproduct 24 is not a silanol condensation product yet was formed from an intermolecular

siloxane interchange reaction of diene 21 producing bis(allyl)-1,1,3,3-tetramethyldisiloxane (15) which was also isolated from the reaction mixture (Figure 4.9).

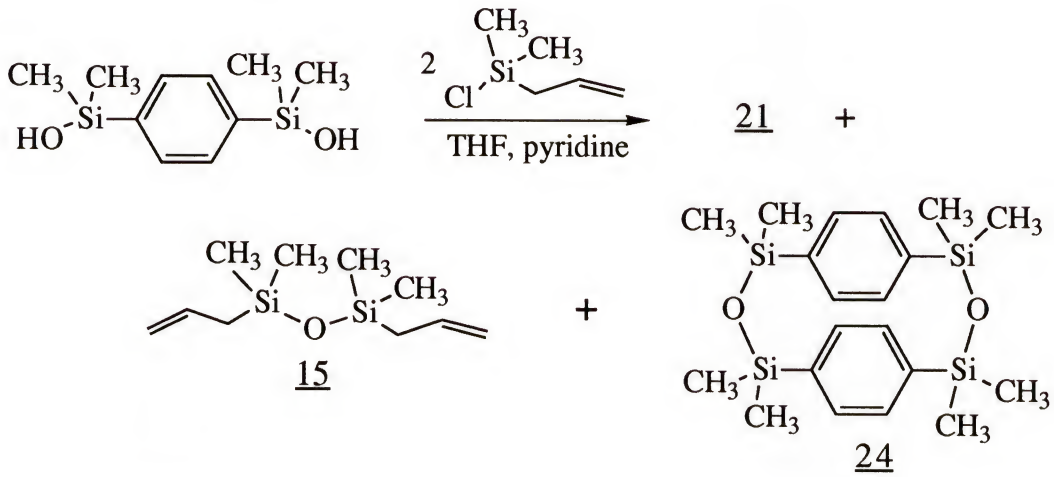


Figure 4.9. Synthesis of monomer 21 and cyclic byproduct 24.

The proposed mechanism for the production of 24 was confirmed by subsequent experiments where neat 1,4-bis(pentamethyldisiloxa)benzene (23) (prepared analogously to the synthesis of 21 with chlorotrimethylsilane) underwent thermal interchange giving cyclic 24, hexamethyldisiloxane, and oligo(tetramethyldisiloxaphenylene) (Figure 4.10). The cyclic byproduct 24 is a potential monomer for ring opening polymerization to poly(disiloxaphenylene), and has been previously sought.[257]

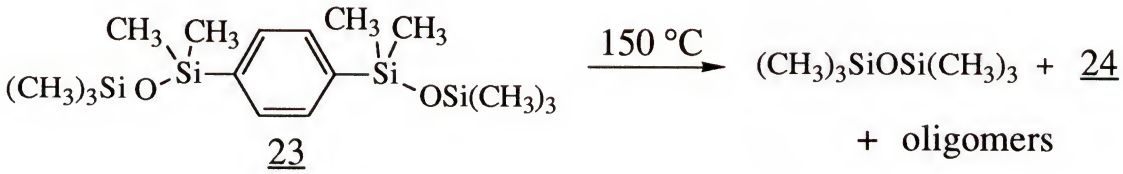


Figure 4.10. Confirmation of thermal siloxane interchange mechanism for production of byproduct 24.

The structure of cyclobis(disiloxa)dibenzene (24) was determined by X-ray crystallography (Figure 4.11). The aromatic rings are parallel, as expected, and are separated by 3.63 Å. The rings are slightly distorted from the ideal 120° angle in benzene in that the C2-C1-C6 and C3-C4-C5 atoms contain an angle of 115.7°. The Si atoms are displaced from the plane of the phenyl rings (inward) by 5.9° and the Si-O-Si angle is an exceptionally large 156.0° which minimizes repulsion of the π-electron clouds of the phenyl rings.

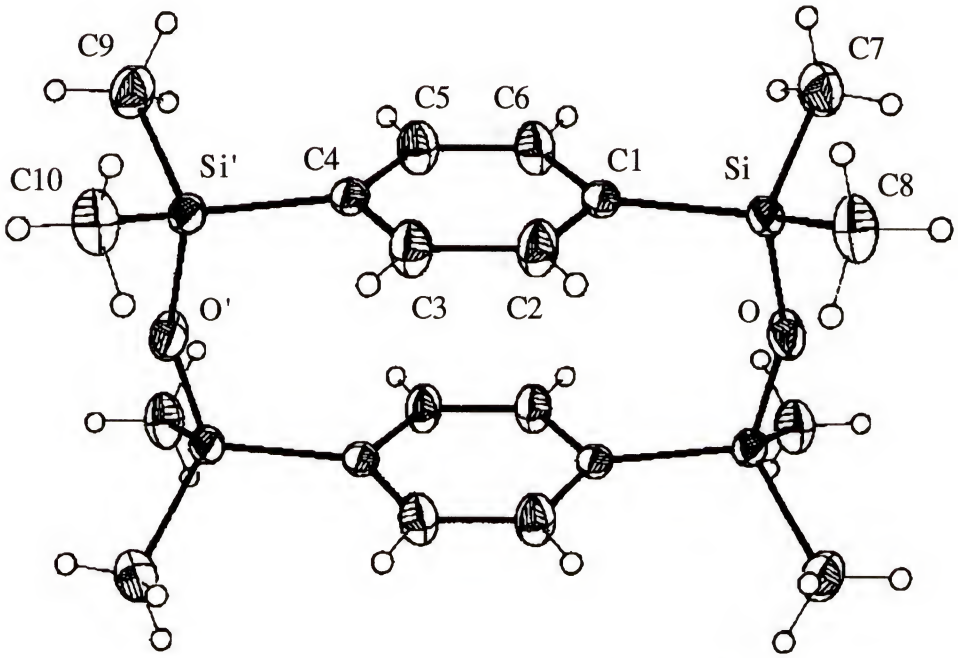


Figure 4.11. Molecular structure of 24 shown with 50% probability ellipsoids, and the atom numbering scheme.

Synthesis of Unsaturated Polycarbosiloxanes

Acyclic diene metathesis (ADMET) polymerization is an equilibrium step propagation condensation type polymerization, where the production and removal of ethylene (when using terminal olefins) drives the reaction. As described previously,[197,235] ADMET polymerizations are performed under step (bulk) conditions and high vacuum with a typical monomer to catalyst ratio of 500-1000 : 1. The ADMET polymerization of carbosiloxadiene monomers is void of side reactions and only pure ethylene is produced. Cyclic products are sparingly present in some cases, due to slow backbiting reactions, as typical for some condensation polymerizations,[208] and are detailed in Chapter 5.

As with the case for the unsaturated polycarbosilanes discussed in Chapter 3, upon initiation of carbosiloxadiene monomers with catalyst 1c, an immediate evolution of ethylene was observed accompanied by a noticeable increase in viscosity within one hour in most cases. Within a few hours after initiation, the use of constant high vacuum (10^{-6} mmHg) was possible for these monomers due to the increase in molecular weight and thereby allowed for the efficient removal of ethylene.

Figure 4.12 displays the ^{1}H NMR spectra for monomer 19 and the reaction mixture of its resulting high molecular weight 79% *trans* polymer 20, and is typical of the clean NMR spectra obtained for these unpurified polymers. Terminal olefin signals were not visible in the ^{1}H NMR as well as the quantitative ^{13}C NMR spectra of polymer 20. Residues of decomposed catalyst 1c are the only impurities in polymer 20 and are too low in concentration to be observed in the ^{1}H and ^{13}C NMR spectra at 200 MHz and 50 MHz, respectively. The multiplet at 5.39 ppm for 79 % *trans* polymer 20 represents the internal vinylic protons from which the *trans* and *cis* isomers are indistinguishable. However, the

cis and *trans* vinylic carbon signals are easily resolved in the ^{13}C NMR spectrum, whereby quantitative experiments provided the accurate determination of the average geometric isomer content.

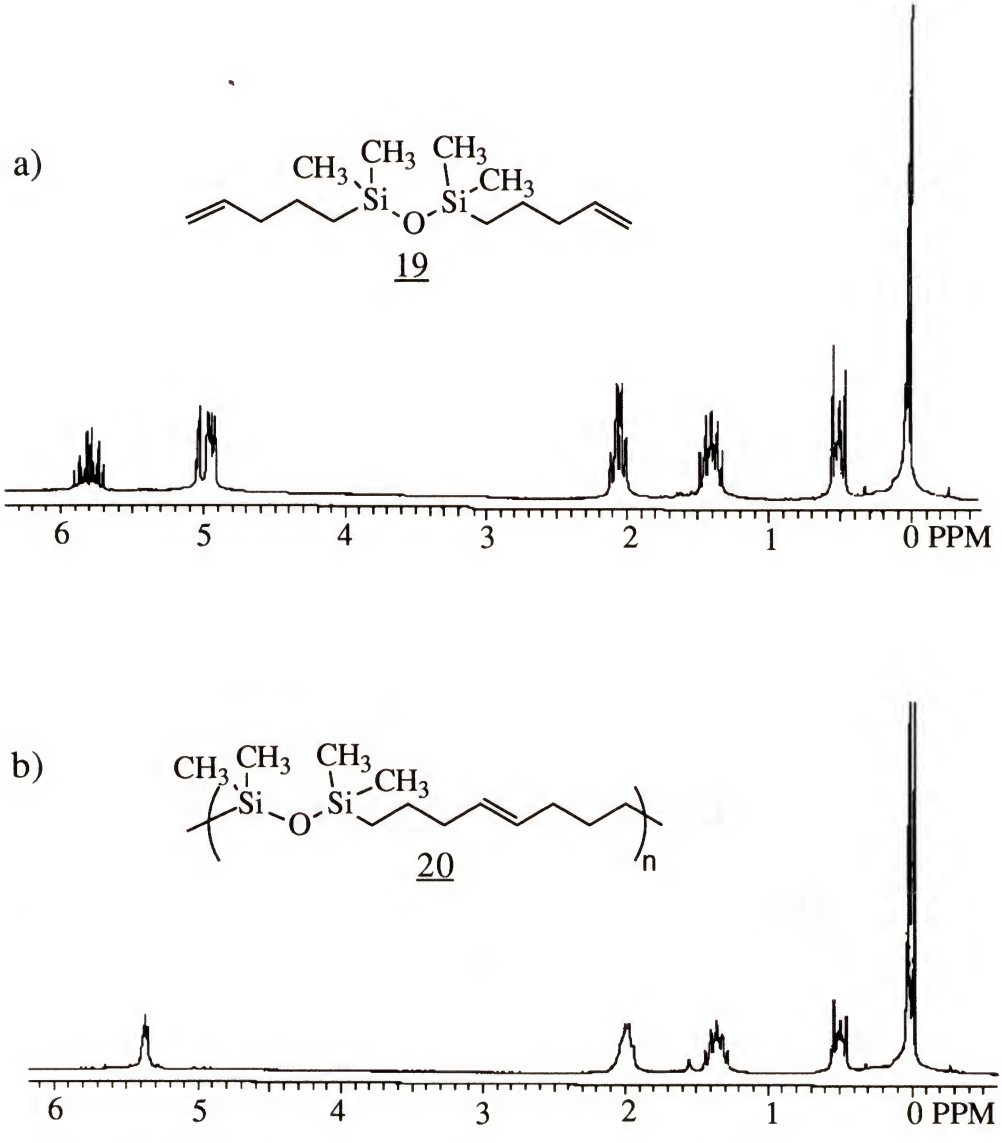


Figure 4.12. ^{1}H NMR spectra for a) monomer 19 and b) 79% *trans* polymer 20.

As was described in Chapter 3, the factor limiting the degree of polymerization for ADMET chemistry, in some cases, is the thermal stability of the catalyst. Although the molybdaneophenylidene, 1 c ($ArN(RO)_2Mo{=}CHCMe_2Ph$), has been observed in solution at temperatures

approaching 85 °C,[252] it is technically a catalytic precursor. Upon initial reaction with a terminal olefin, the more reactive molybdamethylidene ($ArN(RO)_2Mo{=}CH_2$) is generated and remains the only recyclable catalytic species throughout the polymerization, when using vinyl monomers. The methylidene complex is less stable than its precursor, 1c, and can decompose at lower temperatures, and therefore limits the polymerization temperature. However, as in the case for the unsaturated polycarbosilanes (presented in chapter 3), these polycarbosiloxanes remain viscous oils at room temperature, thereby allowing for reasonably high molecular weight polymers to form at low temperature. Table 4.1 contains some of the physical data for the unsaturated polycarbosiloxanes 18, 20, and 22 shown in Figure 4.7. The chain extended polycarbosiloxane, 26 (Figure 4.13), which will be introduced in a later section, is included in Table 4.1 for completeness.

Table 4.1. Polycarbosiloxanes prepared via ADMET polymerization.

Polymer	M_n[a] (GPC)	M_n (NMR)	M_w/M_n[d]	% Trans[b] (NMR)	T_g[e] (°C)	TGA[d] N_2(Air)
18	15000	-	1.7	65	-97	398 (284)
20	32000	-	1.7	79	-93	427 (282)
22	1400	1400[b]	1.2	40	-	-
26	38200	29000[c]	1.7	75	-90	435 (287)

[a] Relative to polybutadiene standards. [b]Measured by quantitative ^{13}C NMR (see experimental). [c]Measured by ^{1}H NMR. [d]Reaction mixture. [e]Temperature (°C) upon heating at 5 °C/min. [f]Temperature (°C) at which 10% weight loss occurs.

Number average molecular weights were determined directly, when possible, by quantitative ^{13}C NMR endgroup analysis. This technique has been a reliable

asset to ADMET polymer characterization since polymers produced by this chemistry possess monomodal molecular weight distributions of linear chains terminated with known olefinic endgroups. Quantitative ^{13}C NMR was also essential for the accurate determination of the geometric isomer ratio for these unsaturated polymers. In most cases, the *cis* and *trans* proton signals were unresolved in the ^{1}H NMR spectra at 200 MHz. Relative number average molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using polybutadiene standards. These standards, when applied to the polymers presented here (Table 4.1), gave a much better correlation with the exact M_n determined by quantitative ^{13}C NMR than did the more common polystyrene calibration standards.

For polymers 18 and 20, the molecular weights were high enough so that the concentration of terminal carbons fell below the limit of detection for NMR endgroup analysis. Although the highest molecular weight was obtained from the polymerization of telechelomer 25 to polymer 26 (see Figure 4.13), the degree of polymerization, as calculated by endgroup analysis, reached only 36 before the viscosity of the reaction mixture prevented magnetic agitation, at which time the reaction was terminated. However, the degree of polymerization achieved in polymers 18 and 20 is estimated to be much greater. The molecular weight distributions for ADMET polymerizations typically approach 2, as predicted for step polymerizations,[7,113] and high average *trans* content polymers are normally produced due to trans-metathesis, or interchange reactions which occur throughout the polymerization.

Aromatic polycarbosiloxane 22 possesses the lowest number average molecular weight for the series and, likewise, the lowest average *trans* content (Table 4.1). The low molecular weight of 22 is most likely due to poisoning of the catalyst by some impurity which eluded repeated purification attempts. Ethylene

evolution was observed upon treatment of monomer 21 with catalyst 1c, yet stopped after several minutes, and attempts to reinitiate with subsequent additions of the catalyst failed. The fact that monomer 21 is a solid within the temperature range of polymerization, and thus required solution techniques, may also have been a factor which limited the molecular weight.

Synthesis and ADMET Polymerization of a Diene Telechelomer

The polymerization of α,ω-telechelic diene macromonomer 25 to polymer 26 is the first example of an oligodiene applied to ADMET polymerizations. Telechelic polymers, which are an important class of macromolecules, possess specific functional end groups designed to undergo additional polymerization, or chain extension, to high polymer.[34] Figure 4.13 displays the synthetic scheme used to prepare polymer 26 from commercial materials and Karsted's catalyst.[254] The hydrosilation oligomerization technique was found to be a convenient method of preparing macromonomer 25 and could provide access to a variety of oligomeric dienes containing main chain silicon functionalization.

Hydrosilation polymerization, first reported by Curry,[68,69] has become a popular route to novel silicon polymers, as well as telechelic polymers,[70-75] and has stimulated considerable efforts in unique applications for metal catalysis in general.[74] Catalytic hydrosilation chemistry was initially developed based on high oxidation state Pt catalyst such as chloroplatinic acid, $H_2PtCl_6(H_2O)_6$; however, catalytic systems involving Pt(0) have also been developed and reviewed.[74] In particular, Karstedt's platinum(0) olefin complex has received recent attention concerning its exact structure.[273,274] This vinylsiloxane olefin adduct was shown to exist as the tris olefin complex depicted in Figure 4.13 and provided a clean and mild route to the β-adduct isomer of telechelic diene 25. ^{13}C

NMR attached proton test (APT) spectroscopy was used to confirm that the pure β-adduct isomer of 25 had been obtained and like monomer 19, methine or methyl carbon signals were not detected in the APT spectrum at 50 MHz. Furthermore, resonances indicative of the Si-H group present in the starting material were not detected by ^{1}H NMR or ^{29}Si NMR spectroscopy, indicating that near quantitative hydrosilation conversions were achieved.

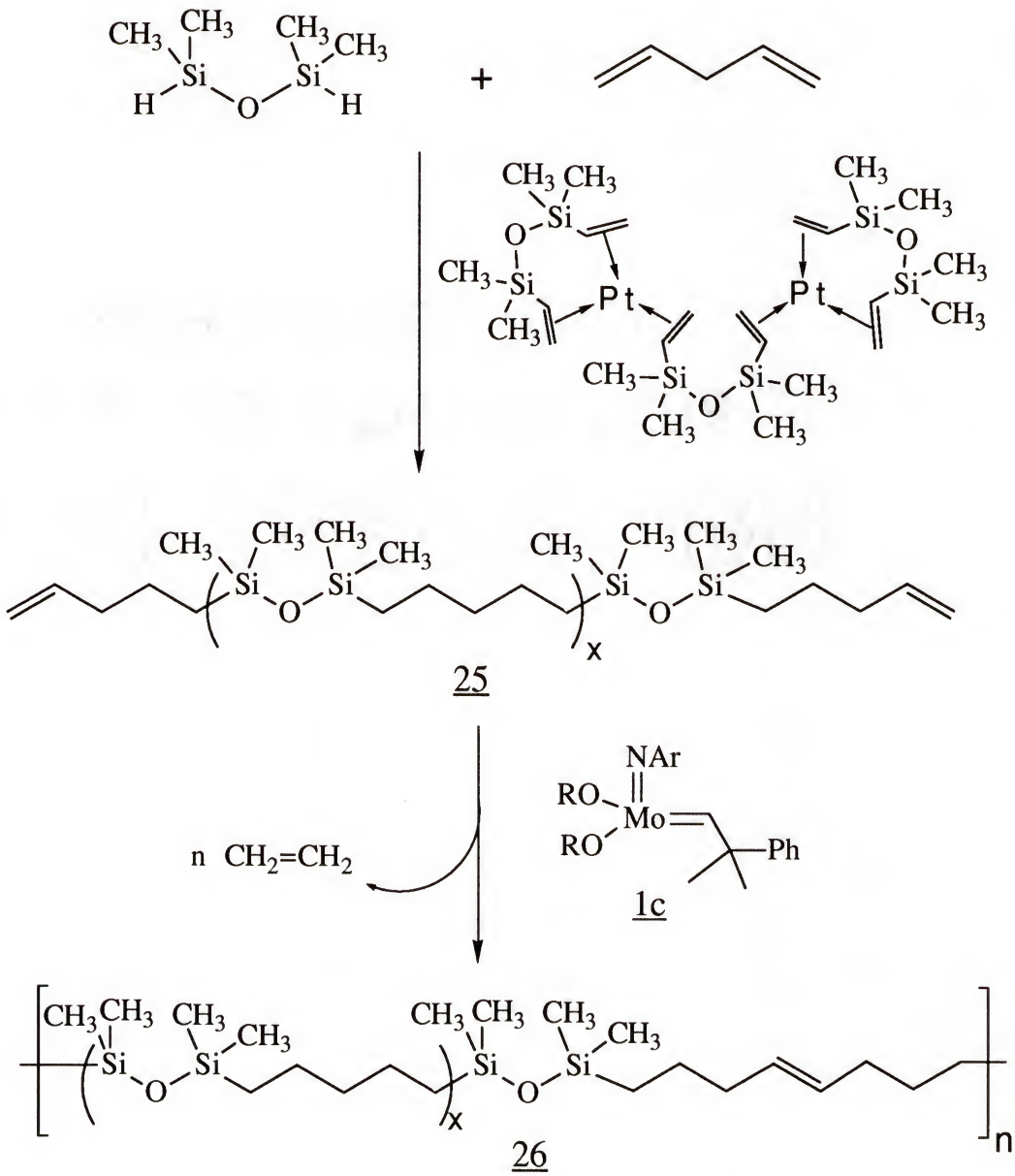


Figure 4.13. Synthesis of α,ω-telechelomer 25 and resulting polymer 26.

Telechelomer 25 was very well defined and contained an average degree of polymerization (DP) of 3.4 by quantitative ^{13}C NMR spectroscopy which corresponds to M_n = 960. These data agree well with results obtained from elemental analysis. According to gel permeation chromatography (GPC) analysis (relative to polybutadiene standards), a number average molecular weight of 550 was measured for telechelomer 25 compared to a M_n = 920 obtained when using poly(dimethylsiloxane) standards (see experimental). Telechelic diene 25 is an ideal monomer for ADMET polymerization since it is a nonvolatile quick flowing liquid. This feature allows for the use of continuous high vacuum at these polymerization temperatures which permits efficient removal of ethylene. Figure 4.14 illustrates the increase in molecular weight from telechelomer 25 to polymer 26 by GPC.

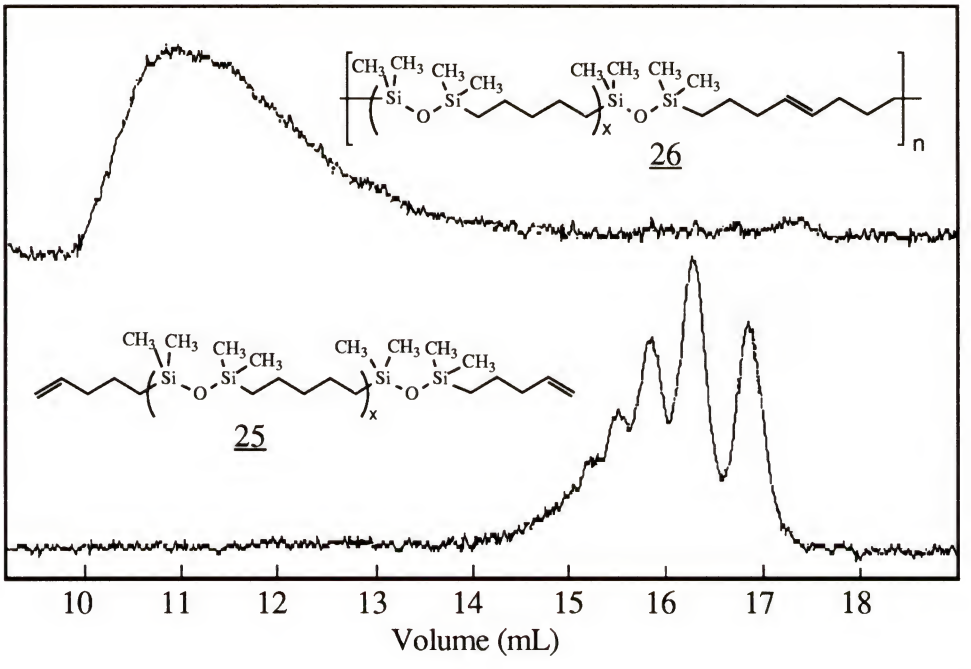


Figure 4.14. Gel permeation chromatography (GPC) of α,ω-telechelomer 25 and resulting polymer 26.

It is clear from the GPC trace of 25 and 26, that individual oligomers are partially resolved in the lower chromatogram representing telechelomer 25, yet are averaged as ADMET condensation ensues (upper trace), giving a more Gaussian molecular weight distribution approaching 2 for high molecular weight polymer 26. Low molecular weight residual starting material (oligomer 25) is not detected in the GPC trace of polymer 26 indicating the high purity and complete functionalization of telechelomer 25.

Figure 4.15 displays the quantitative 50 MHz ^{13}C NMR spectrum for the reaction mixture of 75 % *trans* polymer 26. Every non-equivalent carbon in this macromolecule is easily identified, and the spectrum exemplifies the absolutely clean mechanism by which ADMET polymerization proceeds. The carbon signals contained within the disiloxapentylene linkages (signals 2-4) are clearly visible in the ^{13}C NMR spectrum, as well as the octenylene carbon signals (5-8).

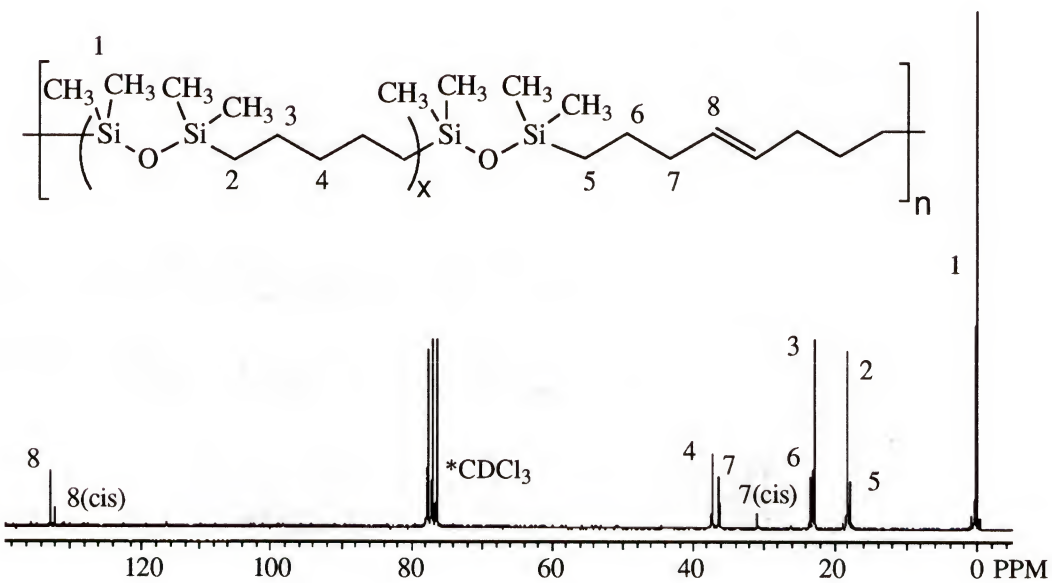


Figure 4.15. Quantitative 50 MHz ^{13}C NMR spectrum of polymer 26.

Polycarbosiloxane Thermal Properties

Differential scanning calorimetry (DSC) was used to determine the glass transition temperatures (T_g) for the high molecular weight polymers 18, 20, and 26 (Table 4.1). Low glass transition temperatures were observed for the polymers as expected for systems incorporating the very flexible -Si-O-Si- linkage.[20] In addition, the alternating siloxane linkage along the backbone of poly(dialkylsiloxanes) are effectively "shrouded" by the organic substituents which prevent inter-chain aggregation. This lack of inter-chain ordering interactions lowers the energy required to bring about segmental motion (i.e., glass transition) between the chains (Figure 4.16).

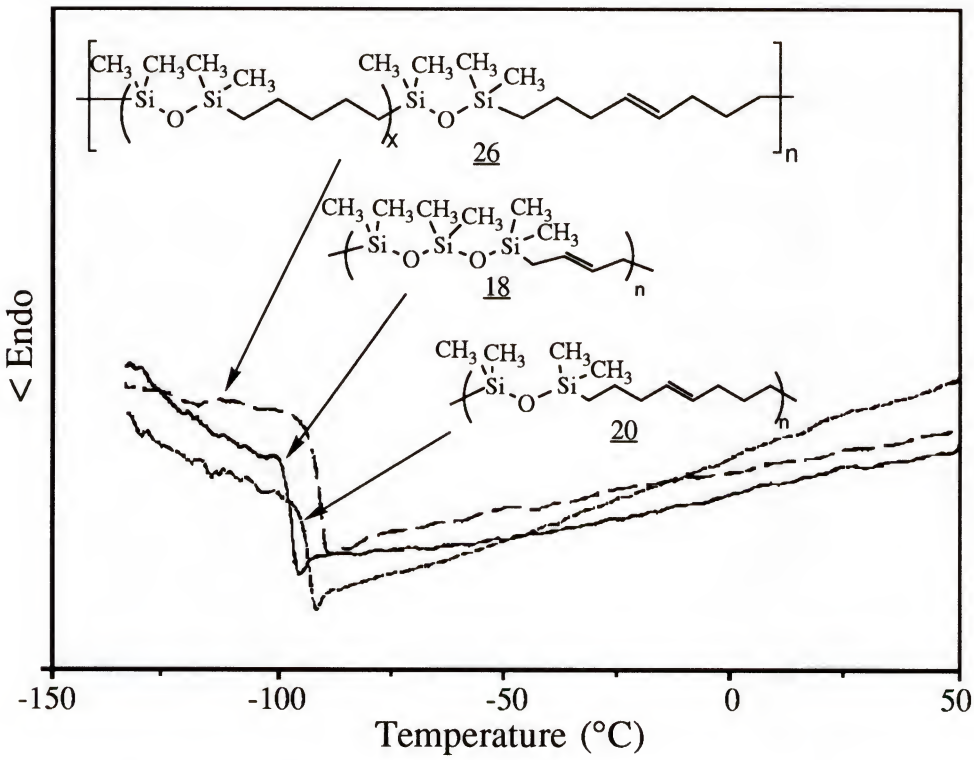


Figure 4.16. Differential scanning calorimetry (DSC) of polymers 18, 20, and 26: scan rate 10 °C/min.

Figure 4.16 contains the DSC thermograms for polymers 18, 20, and 26, indicating glass transition endotherms ranging from -97 to -90 °C upon heating. These properties, when contrasted with the low tempertature behavior of the unsaturated polycarbosilanes presented in chapter 3 (T_gs from -47 to -67 °C, Table 3.2), illustrate the great enhancement in flexibility observed with siloxanes. The T_gs were reproducible, with little deviation, upon cycling at differing scan rates from 10 to 1 °C/min. Melting transitions, as expected, were not observed for these high *trans* content siloxane polymers below 200 °C.

Thermal gravimetric analysis (TGA) was used to measure the thermal stability and extent of thermal decomposition for polymers 18, 20, and 26 (Table 4.1) in nitrogen and in air environments. As discussed in chapter 1, polysiloxanes are also quite thermally stable polymers,[38] primarily attributed to the strength of the Si-O bond (471 kJ/mol vs. 340 kJ/mol for C-O, see Table 1.2). Materials based on siloxane polymers constitute a broad class of high temperature elastomers and plastics and are of considerable recent importance.[38-45]

Figure 4.17 displays a typical TGA thermogram, in both mediums, for polymers 18, 20, and 26. All three polymers retained nearly 100% of their original mass while approaching 400 °C followed by rapid and complete decomposition in nitrogen. Weight loss in air began much sooner, as expected, followed by a slower and more complex mode of decomposition. Similar to the behavior of the polycarbosilanes in chapter 3, these siloxane polymers did not decompose completely in air where typically ca. 10 % weight remained at temperatures exceeding 700 °C (Figure 4.17).

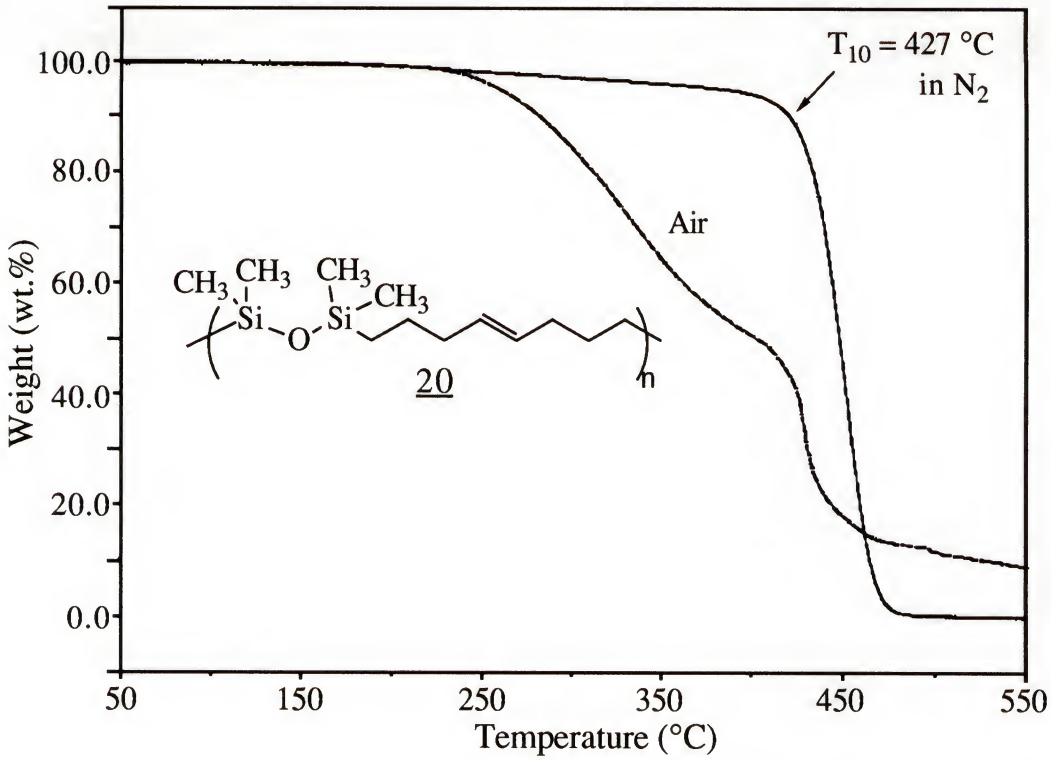


Figure 4.17. Thermogravimetric analysis (TGA) of polymer 20 in N_2 and air: scan rate 10 °C/min,

As was the case for the polycarbosilanes presented in chapter 3, the complete elimination of weight, for all three polymers, in nitrogen, over a temperature range of about 50 °C (5 minutes) perhaps indicates that few decomposition pathways are occurring. Efforts to identify the thermal decomposition products of these polycarbosiloxanes have revealed that cyclic products are generated, as expected. In particular, the thermal decomposition of polymer 18 in nitrogen produces cyclic compound 29, along with other unidentified products (Figure 4.18). Cyclotrisiloxalkene 29 was detected by GC/MS (m/z = 260) analysis of the decomposition products from polymer 18, and was identified by comparison with the mass spectral data of an authentic sample of 29 obtained from a metathesis backbiting reaction discussed in the next chapter. The production of cyclic 29 can be rationalized based on the ease in which other siloxane polymers redistribute to

form cyclosiloxanes upon thermolysis.[19-21] Figure 4.18 illustrates how the intermolecular siloxane interchange or redistribution mechanism may occur for polymer 18.

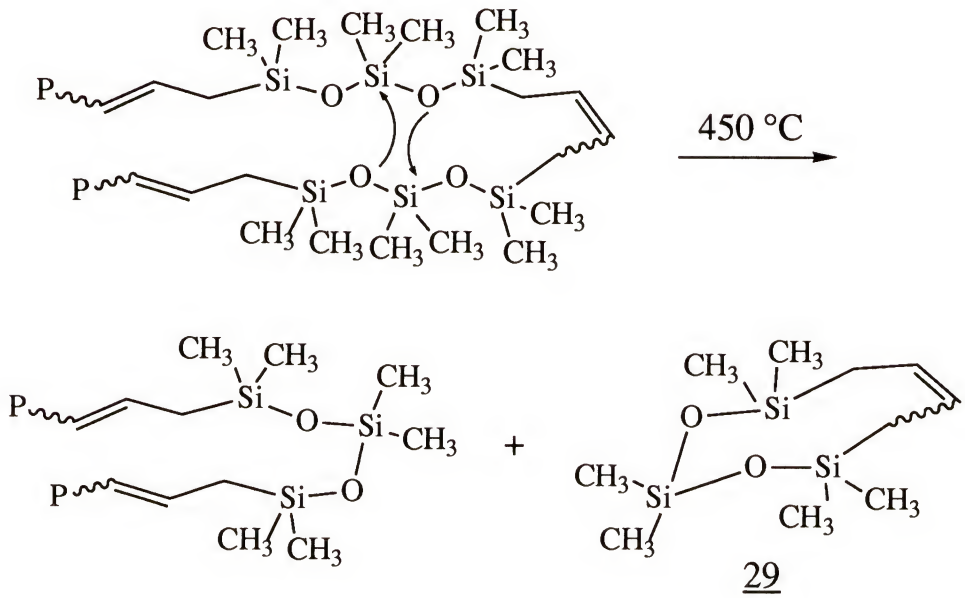
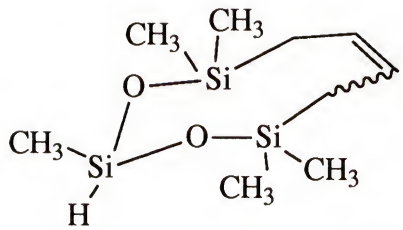


Figure 4.18. Production of 29 from the thermolysis of polymer 18 (P = polymer).

An additional major component present in the decomposition product mixture from the thermolysis of polymer 18 possessed a mass of 246 a.m.u.. Although the true identity of this product is not known, it is perhaps a silane derivative of 29 (shown below) where a silylmethyl hydrogen has migrated to silicon with the extrusion of methylene to give the observed mass. Rearrangements of this kind are well known for poly(dimethylsilanes) which undergo hydride migration at 450 °C with methylene insertion into an adjacent Si-Si bond, as described in chapter 1 (Figure 1.7).[51] Methylene insertion into the adjacent siloxane bond of 29, however, is less likely due to the greater strength of the Si-O bond compared to the Si-Si bond.[28]



Conclusions

Acyclic diene metathesis (ADMET) polymerization now provides access to a new class of polymers which are defined as unsaturated polycarbosiloxanes. The use of a highly active molybdenum alkylidene catalyst facilitates a clean polymerization path to structurally pure linear polymers with low glass transition temperatures and good thermal stability.

Monomer structural designs have been developed which exceed limitations found with divinyltetramethyldisiloxane and obviate the exclusive monomer cyclization exhibited by bis(allyl)tetramethyldisiloxane. By extending the methylene units or the siloxane linkage within the monomer, ADMET polymerization occurs readily while continuously releasing pure ethylene.

The hydrosilation reaction provides a convenient route to a well defined α,ω-diene telechelic oligo(carbosiloxane) which ADMET polymerizes cleanly to high molecular weight.

This new class of functionalized siloxane polymers provides perfectly alternating sites of unsaturation which may be of use for preparing well defined modified systems such as, graft copolymers and cross linked elastomers. The good thermal stability of these polycarbosiloxanes coupled with their low glass transition temperatures illustrates the extreme use temperature range typical of siloxane polymers and that incorporation of significant degrees of carbon linkages did not completely sacrifice these properties.

CHAPTER 5

POSTCONDENSATION REACTIONS IN ADMET CHEMISTRY

Acyclic diene metathesis chemistry propagates via an equilibrium condensation mechanism, whereby the evolution and removal of a small alkene condensate drives the equilibrium to high polymer when linear structures are favored.[197,232,235,252] As discussed in Chapter 1, the mechanism, first proposed by Wagener, Boncella, and Nel (Figure 1.43),[235] is supported based on the following consistent experimental evidence: 1) ethylene is continuously produced during the reaction, 2) high molecular weight polymer is not observed at low monomer conversions, 3) unpurified polymer reaction mixtures exhibit monomodal molecular weight distributions approaching 2, 4) molecular weight determination by end group analysis (NMR) compare well with colligative property measurements (VPO) and relative measurements (GPC), 5) the average geometric configuration of ADMET polymer increases in *trans* content as the reaction proceeds, indicative of a dissociative catalysis, 6) an existing ADMET polymer can be polymerized to higher molecular weight or copolymerized with an additional diene by the removal of a monene condensate,[236] and finally, 7) the equilibrium cycle is truly reversible since ADMET polymer can be depolymerized to its original diene monomer by shifting the equilibrium with excess ethylene.[245]

The mechanism is sufficient in explaining how productive metathesis condensation occurs since terminal olefins are contained in every step of the productive cycle (Figure 1.43). In this kinetically controlled regime (high

concentration of terminal olefin present), alkylidene reactions with unsubstituted (terminal) olefins is favored over inter-chain redistribution reactions or other degenerate equilibria. However, when terminal olefin concentration decreases near the end of the polycondensation reaction, competing equilibria involving the excess internal olefins within the polymer are significantly enhanced, and a "resting state equilibrium" is established. Metathesis reactions which occur in this thermodynamic regime are considered here.

This chapter presents some results concerning the postcondensation resting state behavior of the polycarbosilanes and polycarbosiloxanes presented in Chapters 3 and 4, respectively. At the postcondensation resting state where ring/chain equilibria can occur, cyclization reactions for some polymers are observed. Statistical theory of ring/chain equilibria in polymer chemistry has been developed by Jacobson and Stockmayer in 1950,[207] and is characteristic of many polymerization reactions, including ROMP.[208] In particular, more recent work by Höcker,[209-213] devoted detailed experiment toward delineating the predicted theory of ring/chain equilibria in ROMP chemistry. As will be shown, cyclizations which occur during ADMET polymerizations are the result of slow backbiting reactions when cyclic products are favored.

Thermodynamic Considerations of Metathesis Polymerizations

Ring opening metathesis polymerization (ROMP) using Schrock type alkylidene catalysts (1, Figure 3.1) is considered to proceed irreversibly in a "living" manner, for some cases, as described in Chapter 1.[185] The rate for the reaction of alkylidene with cycloalkene monomer and subsequent ring opening is much faster than any competing degenerate metathesis equilibria, and therefore are "living" propagation mechanisms. The propagation of acyclic dienes in a

condensation manner, on the other hand, envelopes many complexities which ROMP avoids.

The thermodynamic concepts of ring opening polymerizations, in general, are well known and have recently been summarized by Ivin.[205] Polymerization is typically enthalpy driven due to the release in bond angle ring strain in small rings and non-bonded strain for large rings resulting from intra-ring atomic interactions. For very large (oligomeric) rings, containing negligible strain, polymerization is entropy driven, through the gain of translational entropy in the polymer.

Although the mechanisms of propagation are very much different within the kinetically controlled regime of the polymerization, ADMET and ROMP share the same thermodynamically controlled later stages of polymerization. In this regime, monomer is completely consumed for the case of ROMP and condensation is negligible for the case of ADMET polymerization, and ultimately the situation is indistinguishable, consisting, namely, of a mixture of unsaturated polymer and active metathesis catalyst.

For a given monomer to catalyst ratio, the reversible propagation reaction in ADMET polymer chemistry is dependent upon the concentration of condensable, i.e., terminal, alkene and the extent by which competing equilibria interfere with productive intermediates, assuming polymerization is performed in the bulk, and catalyst activity remains constant. The overall free energy (ΔG) of ADMET polymerization,

$$\Delta G = \Delta H - T\Delta S$$

is negative due to the slightly negative change in enthalpy (ΔH) gained from the conversion of a terminal to an internal olefin, and, presumably, a positive change in entropy (ΔS) due to the liberation of a gas - ethylene in most cases. However, the entropy term may be more largely dependent on the diene monomer, and has not been shown to be positive for ADMET polymerizations in general. The

entropy term may be negative by the small amount equal to the difference in entropy gained by the evolution of a gas and that lost by the formation of a macromolecule (i.e., the loss in translational entropy of the monomer).[205]

Catalyst concentration ultimately affects the molecular weight in ADMET polymerizations by dictating when condensation ends or becomes negligible. When the concentration of active catalyst species, composed of alkylidene/metallacycle equilibria, becomes sufficiently greater than (or consumes) the concentration of condensable terminal olefin, propagation ends and degenerate equilibria, or ring/chain equilibria when favorable, are dominant. In the extreme case, terminal olefin consumption, and thus condensation, is complete and the molecular weight is given by the initial monomer to catalyst ratio. For all practical purposes however, the limiting theoretical molecular weight is never achieved in ADMET polymerizations since, presumably, propagation eventually becomes too slow relative to the reasonable lifetimes of the alkylidene/metallacycle species.

Postcondensation Resting State Equilibria

The favored postcondensation resting intermediate of the catalyst is not known for the unsaturated organosilicon polymers detailed in Chapters 3 and 4. Postcondensation equilibria composed of various substituted metallacycle and alkylidene species are perhaps stabilized through coordination by electron rich groups. Coordinative stability could result from nearby internal olefins, as referred to in Chapter 1 (Figure 1.33), or from Lewis basic atoms such as the siloxane oxygen contained in the polycarbosiloxanes presented in Chapter 4. Coordination of polar groups to the metal contained within a metallacycle has previously been shown for catalyst 1 in the presence of more basic carbonyl[189]

and amine[199] containing olefins. Alkylidene reactivity has also been proposed to be a function of favorable intermolecular olefin/metal complexes, as discussed in Chapter 1 (Figure 1.35).[206] Despite the true identity of the favored post condensation intermediate, every (degenerate) equilibrium, which exists after the concentration of terminal olefins falls below that necessary for competing condensation, contains a polymer chain terminated alkylidene (Figure 5.1).

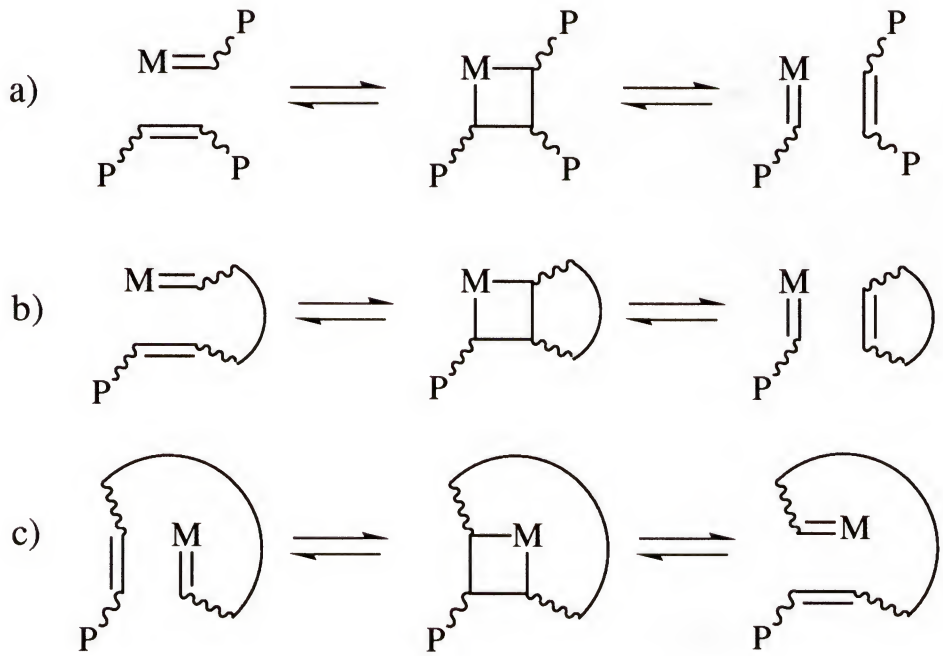


Figure 5.1. Postcondensation equilibria for unsaturated polymer, P, and catalyst M=M(N-2,6-C_6H_3-*i*-Pr_2)[OCMe(CF_3)$_2$]$_2$ (M=W(1a,b), Mo(1c)).

Figure 5.1 illustrates three generalized equilibria which are possible during the resting state, after ADMET condensation (or ROMP addition) has ceased. Equilibrium a) describes inter-chain degenerate metathesis, while b) and c) represent intra-chain cyclic forming reactions (i.e., back biting), and intra-chain degenerate reactions, respectively. If the terminal alkylidene should choose to add to the nearest internal olefin within the chain on which it is attached (which should be kinetically favored vs. more distant double bonds), then a tri-substituted

intermediate metallacycle would form and, upon nondegenerate cleavage, produce a cyclic containing a single repeat unit (Figure 5.1b). Therefore repeat units of a kinetically advantageous length would favor cyclization due to a back biting reaction.

Polycarbosilane Back Biting Reactions

Cyclic byproducts were observed in the case of polycarbosilanes 4 and 6 (Figure 3.4) presented in Chapter 3, and were only detected at the very end of the polymerizations when using the tungsten alkylidene 1 ($RCH{=}W(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$, Figure 3.1). Under these conditions, the molar concentration of condensable terminal olefin had become negligible since the evolution of ethylene was no longer observed. At this stage in the polymerization, a resting state equilibrium had been reached, by definition, since productive polycondensation had ended, as discussed above.

The polymerization of diallyldimethylsilane (3) to polymer 4 (Figure 3.4) produced trace (< 1mol%) quantities of the cyclic dimer, 1,1,6,6-tetramethyl-1,6-disilacyclodeca-3,8-diene (27) (Figure 5.2). Dimer 27 sublimed as a white solid directly from the polymer reaction mixture under high vacuum. The formation of this ten-membered ring is due to a slow back-biting reaction since no dimer is collected until the end of polymerization when intra-, as well as degenerate inter-chain metathesis is undoubtedly occurring. Cyclic 27 is only produced during the postcondensation resting state, further, since a favorable dimerization early in the reaction would have precluded polymer formation. Figure 5.2 illustrates the back biting mechanism for polymer 4 and the formation of cyclic dimer 27.

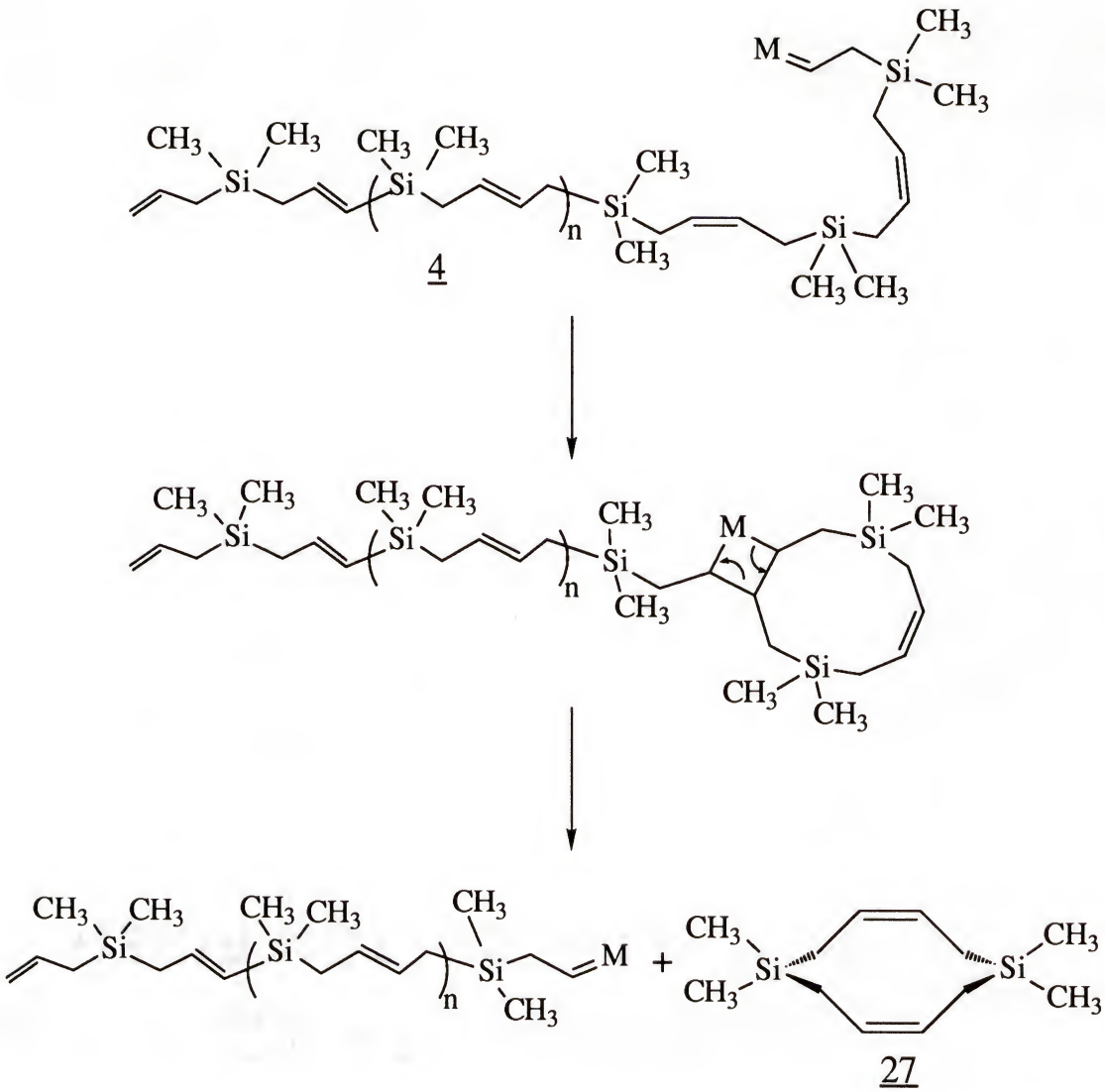


Figure 5.2 Back biting mechanism for formation of cyclic dimer 27 from polymer 4. M = W(N-2,6-C_6H_3-*i*-Pr_2)[OCMe(CF_3)$_2$]$_2$.

The formation of cyclic compound 27 from a back biting reaction of polymer 4 was subsequently confirmed by other researchers using Schrock's molybdenum catalyst 1c (Figure 4.1).[255] These workers found that diallyl monomer 3 polymerizes in solution to an equilibrium mixture of polymer 4 and the cyclic dimer 27. The same equilibrium mixture was also reportedly observed when various substituted silacyclo-3-pentenes were catalyzed by 1c. These researchers did not, however, mention that byproduct 27 was formed when polymerizing

monomer 3 in the bulk, yet a back biting mechanism identical to that depicted in Figure 5.2 was proposed for the reactions carried out in solution.[255] All three of the possible isomers of dimer 27 (*cis,cis*, *cis,trans*, and *trans,trans*) were reported to have been observed for the solution polymerizations,[255] whereas only the pure *cis,cis* isomer is formed under ADMET bulk conditions. These results are expected for solution mediated metathesis, as will be shown in the following sections involving back biting reactions of an unsaturated polycarbosiloxane.

It is clear that polymer 4 prefers to back bite and form the 10-membered disilacycloalkene 27, at equilibrium, instead of the kinetically favored, yet more strained, dimethylsilacyclopent-3-ene. The 5-membered ring was not observed during the ADMET polymerization of monomer 3. The favorable formation of cyclic diene 27 can be attributed to its notable structural stability. The crystal structure was determined for the tetraphenyldisila derivative of dimer 27 by the researchers above, where the molecule was shown to adopt an "arm-chair" conformation (shown analogously as reported in Figure 5.2).[255]

The polymerization of monomer 5 to form polycarbosilane 6 also resulted in the formation (< 1 mol%) of a cyclic byproduct. In this case, polymer 6 chooses to form the liquid 8-membered cyclic compound, 1,1,4,4-tetramethyl-1,4-disilacyclooct-6-ene (28) (Figure 5.3). As was the case for the reaction of diallyldimethylsilane (3), condensation of the cyclic compound 28 was not observed early during the polymerization and was only produced after the viscosity of the mixture reached a maximum (qualitatively), and the condensation of ethylene was no longer observed. Polymer 6, during its postcondensation resting state, is therefore responsible for the formation of the cyclic product, and initial cyclization of monomer is not favorable.

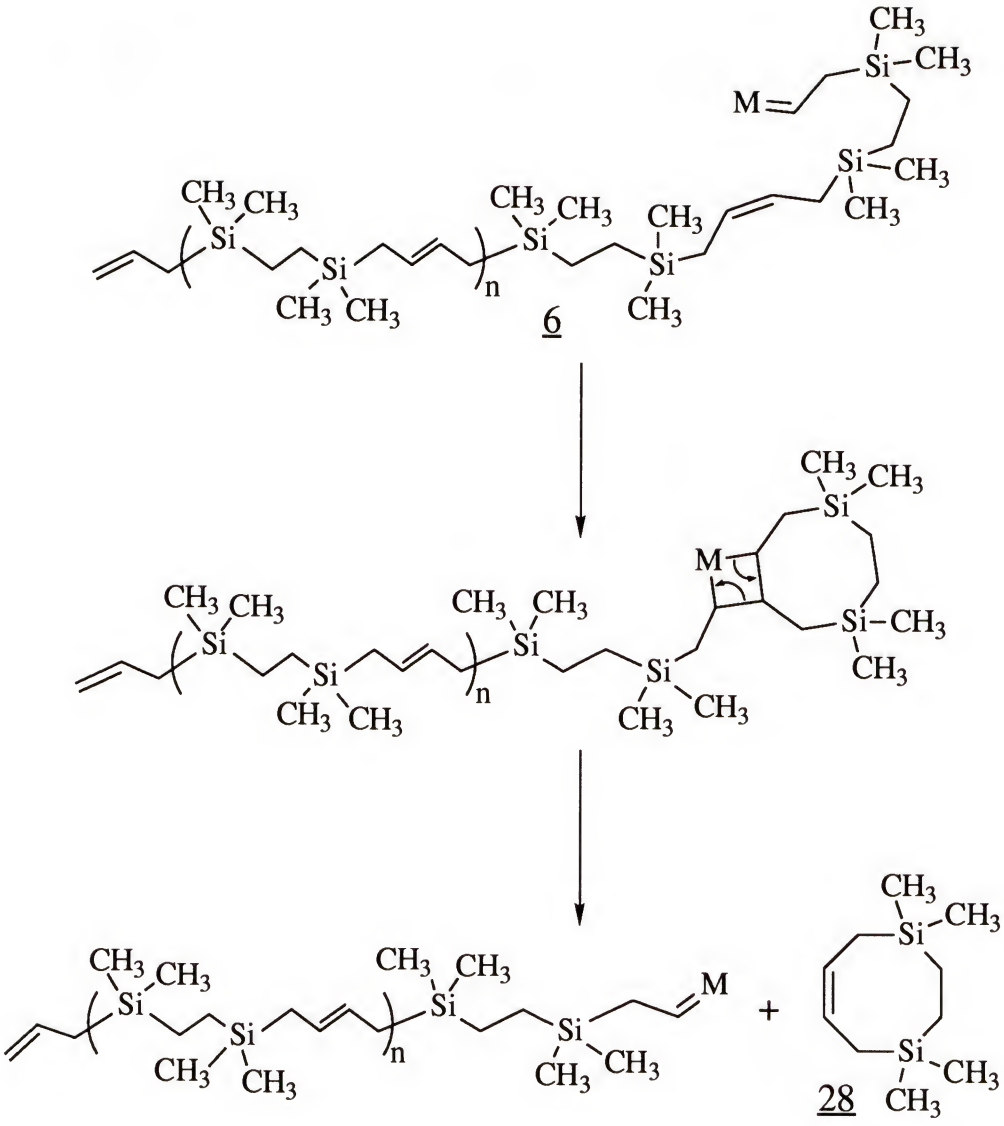


Figure 5.3. Back biting mechanism for formation of cyclic dimer 28 from polymer 6. M = W(N-2,6-C_6H_3-*i*-Pr_2)[OCMe(CF_3)$_2$]$_2$.

Figure 5.4 displays the 200 MHz ^{1}H NMR spectrum for cyclic byproduct 28. Whereas the vinylic and allylic proton signals for polymer 4 and cyclic dimer 27 are essentially identical, the vinylic *cis* proton signals in the more strained 8-membered cyclodisilaalkene 28 are shifted significantly (5.27 ppm vs. 5.38 ppm) downfield from the *cis* vinylic proton signals in the linear polymer 6 (Figure 3.7). Likewise, the allylic proton signals appear at 1.39 ppm, and 1.48 ppm for polymer 6 and cyclic back biting product 28, respectively.

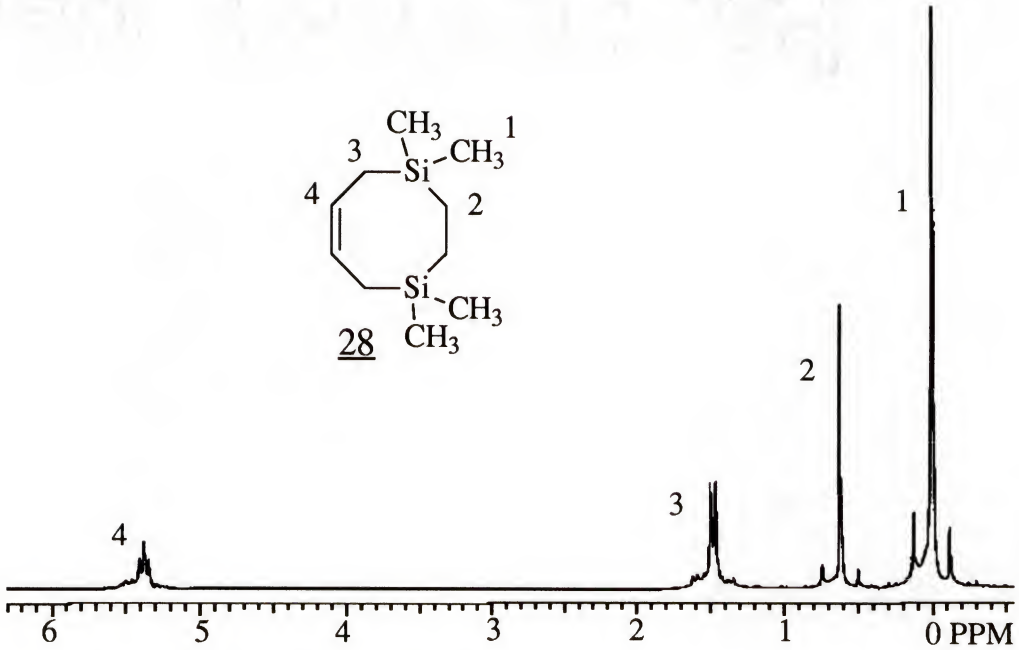


Figure 5.4. 200 MHz ^{1}H NMR spectra of cyclic byproduct 28.

Polycarbosiloxane Back Biting Reactions

The unsaturated polycarbosiloxanes presented in Chapter 4 (Figure 4.7) possess the very flexible siloxane linkage, and like the carbosilane polymers, they are viscous liquids at room temperature. When considering back biting possibilities for the polycarbosiloxanes in the presence of molybdenum alkylidenes produced from catalyst 1c, only the trisiloxabutenylene polymer, 18, and the disiloxaoctenylene polymer, 20, are likely candidates (Figure 4.7). These two polymers possess a repeat unit which would allow 9- and 11-membered rings to form upon back biting. The chain extended polymer 26 would require at least a 35-membered ring and is kinetically disfavored, whereas phenylene polycarbosiloxane 22 did not reach high molecular weight, and therefore a postcondensation equilibrium, where back biting occurs, was not attained. It is now clear that cyclization is not favored for high molecular weight polymer 20,

since no other products were observed during, or after, the polymerization, yet the postcondensation resting state was achieved. The only polycarbosiloxane that undergoes back biting reactions is the trisiloxabutenylene polymer, 18.

Polymer 18 undergoes backbiting to give the 9-membered cyclic product, 29 (Figure 5.5). Unlike those polycarbosilanes which backbite, cyclic 29 was not first observed during the bulk homopolymerization of monomer 29, but was discovered during a solution copolymerization of oligomers of 18 with another diene monomer which is described in Chapter 6. Before this observation, only oligomers of 18 had been obtained due to synthetic difficulties, and cyclic 29 was not detected during the bulk oligomerization of 29. These observations are consistent with the above polycarbosilane results, in that cyclics observed from ADMET polymers result from backbiting reactions and are not present when condensation is a catalytic option.

Once high polymer 18 was obtained, and its postcondensation resting state established, the polymer reaction mixture did contain 7 mol% of the cyclic carbosiloxane, 29. Further, this 9-membered cyclotrisiloxalkene could be generated and removed under high vacuum if the final reaction mixture (after the condensation of ethylene was no longer observed) of polymer 18 was equipped with an efficient condenser. Under these conditions, cyclic 29 was slowly distilled so that 7 mol% was isolated in 5 hours, and the relative concentration (7 mol%) of cyclic 29 remaining in the reaction mixture was unchanged. This constitutes evidence that a slow ring/chain equilibrium had been established under these conditions which removal of 29 slowly advanced.

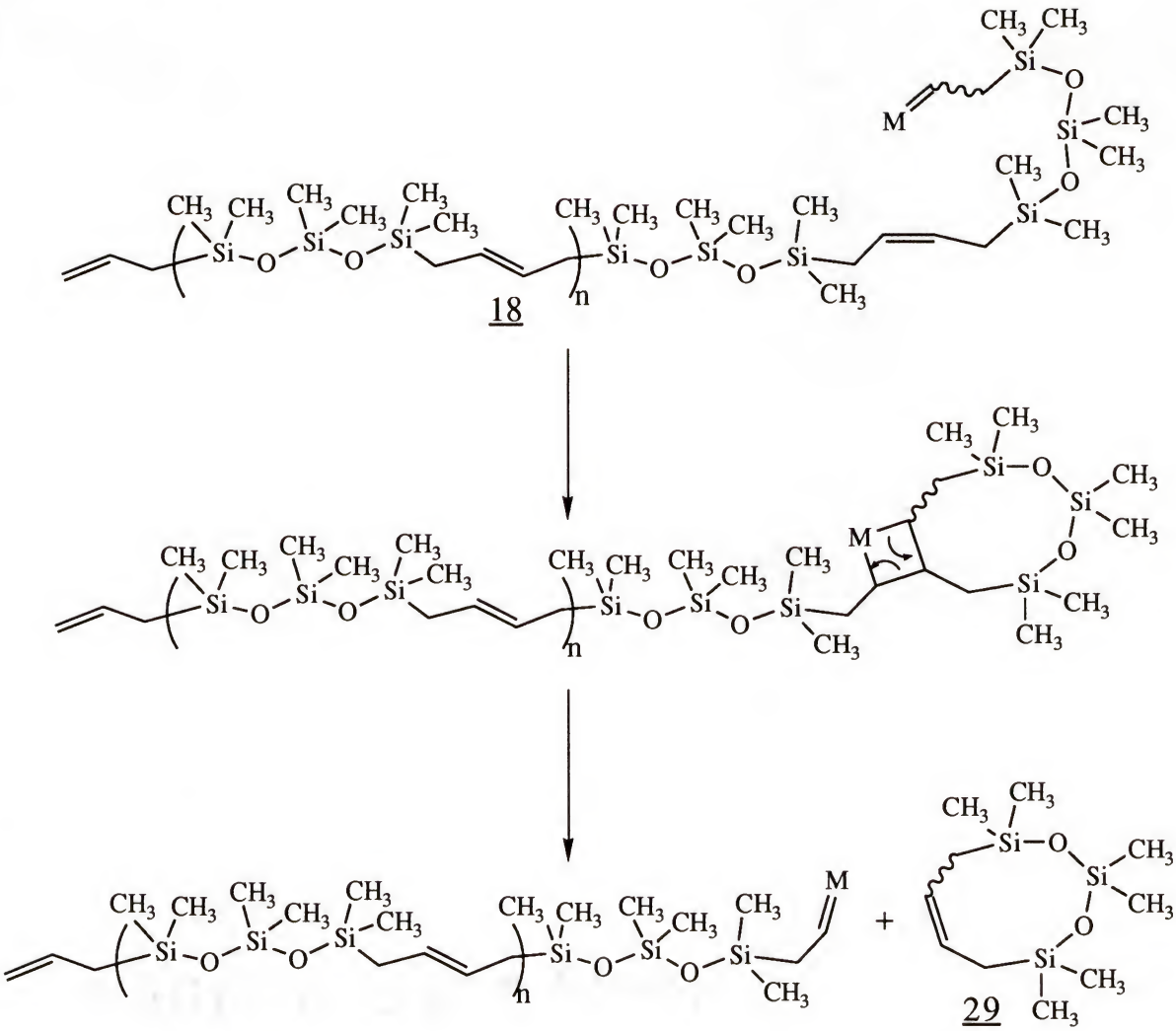


Figure 5.5 Back biting mechanism for formation of cyclic dimer 29 from polymer 18. M = $Mo(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$.

These results complement those reported for classical metathesis systems recently summarized by Ivin.[205] At the resting state equilibrium, after ADMET condensation has stopped, the kinetics of the system (unsaturated polymer containing catalyst) presumably obey those controlling any depolymerizable polyalkenylene containing an active metathesis catalyst. Here, reversible ring opening metathesis polymerization (ROMP) can take place, and the rate of the forward reaction is given by,

$$R_p = (k_p[M] - k_d)[P]$$

where k_p and k_d are the rate constants for polymerization by ROMP and depolymerization by backbiting, respectively, and where [M] and [P] are the respective concentrations of monomer and polymer.[205] Therefore, cyclic 29 is a slow kinetic product, and the rate of intramolecular backbiting (Figure 5.1c) is limited by competing intermolecular degenerate equilibria (Figure 5.1b). The situation changes, and cyclic 29 is nonexistent if an appreciable concentration of condensable terminal olefin is present where condensation polymerization is predominant, as in the case during the oligomerization of monomer 17. Backbiting is not observed, nor expected, during the polymerization of monomers 19 and 21 to polymers 20 and 22 (Figure 4.7), respectively, simply due to the unfavored formation of extremely large cyclic molecules. Jacobson-Stockmayer's theory of ring/chain equilibrium[207] predicts

$$[M] \propto M_X^{-2.5}$$

where [M] is the concentration of the cyclic product at equilibrium and M_X is the number of repeat units in the cyclic product.

The conclusion that the competing intermolecular equilibrium (Figure 5.1a) is the limiting factor for the production of cyclic 29 in the bulk is best supported by the observation that 29 is produced much faster and to a greater extent in solution (Figure 5.6). In an NMR experiment, active polymer 18 was diluted with *d6*-benzene and 36 mol% of cyclic compound 29 was generated within 5 minutes. If simple mobility of the alkylidene terminated chain end was the limiting rate factor for the production of cyclic 29, then upon dilution, all equilibria would increase by the same factor and the observed enhanced cyclization (vs. cyclization in the bulk) would not have been expected. Figure 5.6 summarizes the cyclization results for polymer 18.

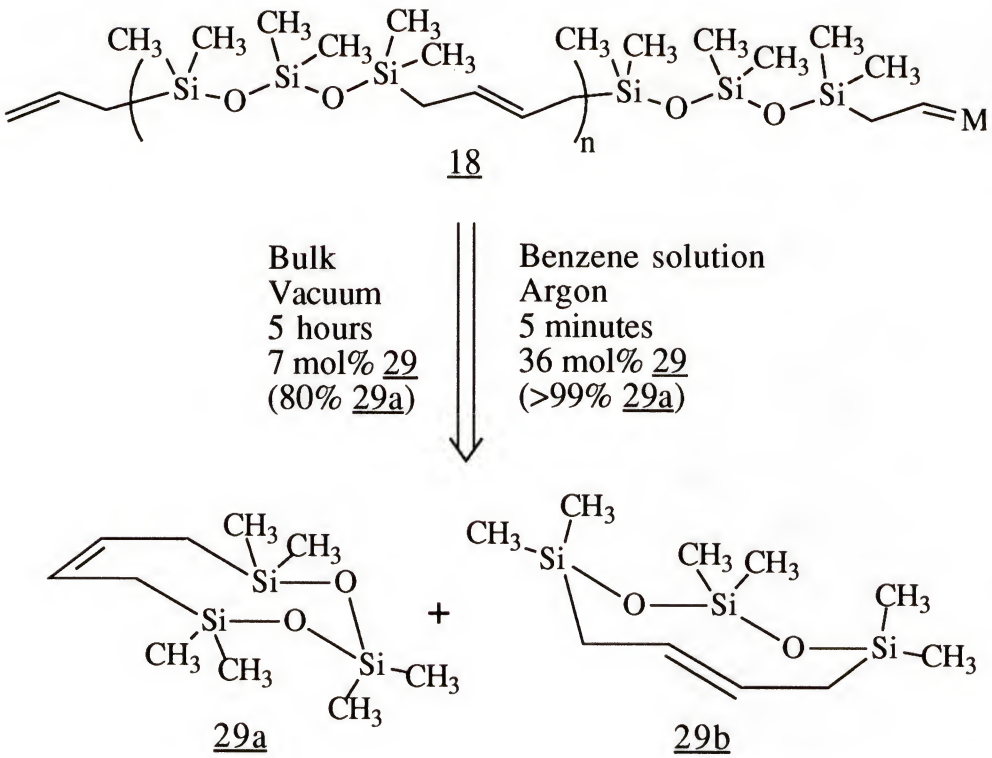


Figure 5.6 Preparation of *cis* (29a) and *trans* (29b) cyclic back biting product 29 from polymer 18. M = Mo(N-2,6-C_6H_3-*i*-Pr_2)[OCMe(CF_3)$_2$]$_2$.

The quantity of cyclic 29, generated from the dilution of polymer 18, did not significantly change over a period of several days at room temperature and may indicate that an equilibrium between linear and cyclic oligomers had been established as predicted by the equation above. The rate of backbiting, or cyclization, should become negligible when [M] ([29] in this case) becomes sufficient for competing ring opening reactions to occur. However, it is unlikely that cyclic 29 is a ROMP monomer, under these conditions, simply because it is produced by backbiting. If cyclic 29 is polymerizable by ROMP, then its ceiling temperature should exist below 25° C, under these conditions. Similar processes have been observed where diallylether bulk oligomerization,[249] and diallylsilane solution polymerization,[255] when using catalyst 1c, established an equilibrium with monomer cyclization. Furthermore, as mentioned earlier, Grubbs and Fu

have shown, very recently, that various diene-ethers[198] and diene-amines[199] will selectively cyclize in solution when catalyzed by 1c.

Interestingly, the bulk isolation of 29 gave an 80 % to 20 % *cis* to *trans* mixture; while during the solution production of 29, the *trans* isomer (29b) (Figure 5.6) was not present in concentrations sufficient to integrate by ^{1}H NMR. It seems reasonable that 29b is produced in solution yet is readily isomerized by polymer terminated alkylidenes to, presumably, the more thermodynamically stable *cis* isomer (29a). Some support for this presumption exists, in that the *cis* isomer is thermodynamically more stable for 7- to 10-membered cycloalkenes, wherein, *cis* cyclononene is favored by 2.8 kcal/mol over the *trans* isomer.[275,276] Furthermore, in the bulk, and especially under conditions where 29a and 29b are being continuously removed, the opportunity for *trans* to *cis* metathesis mediated isomerization is greatly diminished.

Figure 5.7 depicts the ^{1}H NMR spectra for polymer 18 and the mixture of *cis* and *trans* isomers of 29 collected from the bulk reaction mixture of 18. The two (top and bottom) expanded regions represent the internal vinylic protons for polymer 18 and cyclic compound, 29a,b, respectively. These signals illustrate the subtle downfield chemical shift that ring strain induces on the vinylic (as well as the allylic) protons of 29 as compared to the corresponding proton signals in 18. Although not legible in Figure 5.7, it is clear that the *cis* and *trans* isomers of polymer 18 and cyclic 29 also impose different environments on both the non-equivalent methyl substituents in that the *trans* affected methyl protons are slightly shifted upfield from those affected by the *cis* isomer. This effect is also obvious when comparing the methyl substituent signals in the ^{13}C NMR spectra for the two. No other significant differences are observed in the ^{13}C NMR or ^{29}Si NMR spectra between 18 and 29 (see experimental for chemical shifts). The ^{29}Si atom shift similarities, however, are expected since Si atoms contained in large siloxane

rings, e.g., the cyclic tri- and tetrasiloxanes, D_3 (-20 ppm) and D_4 (-22 ppm), respectively, possess nearly the same chemical shifts as for the Si atoms in the D units observed for linear poly(dimethlylsiloxane).[277]

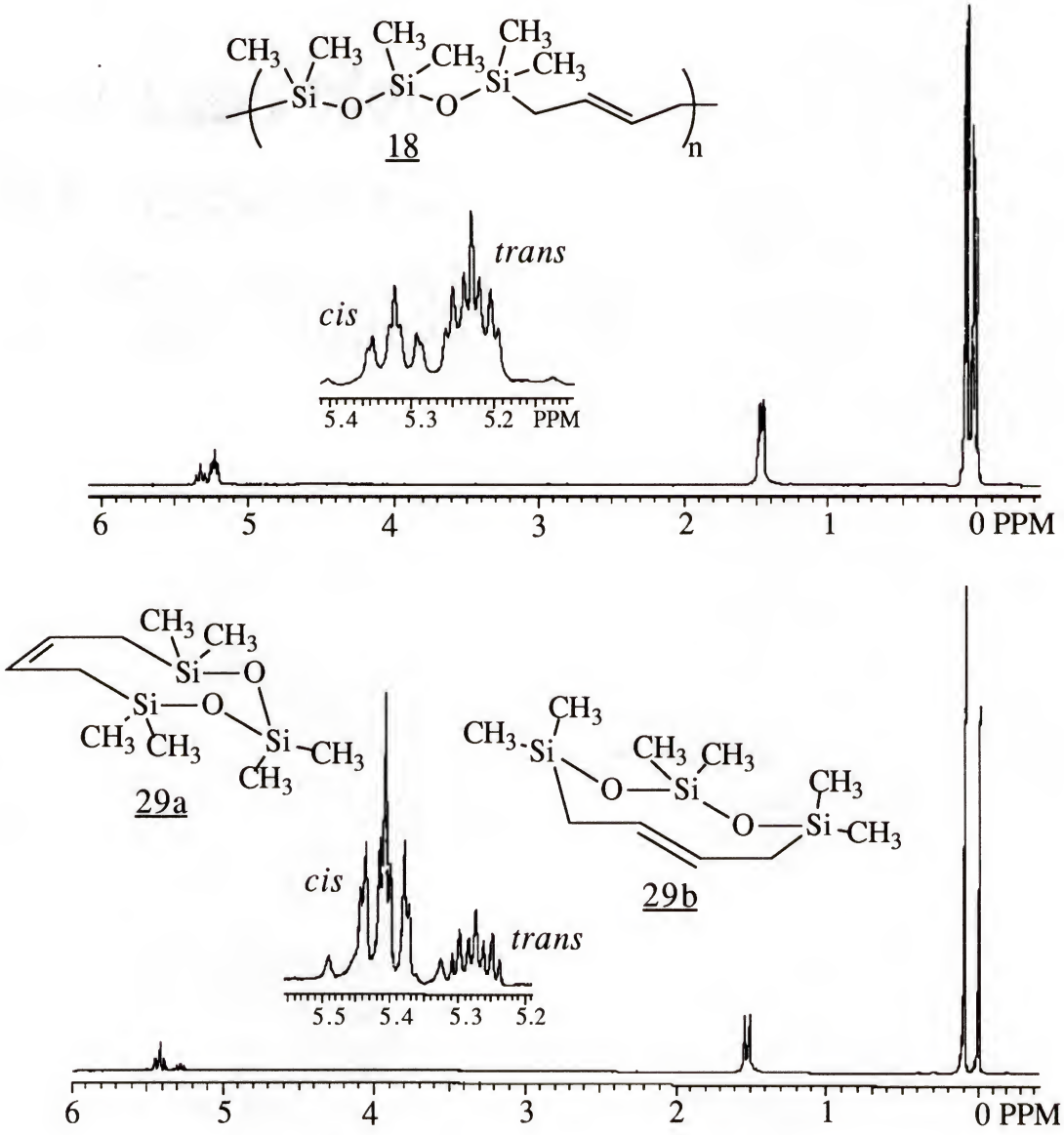


Figure 5.7. 200 MHz ^{1}H NMR spectra of cyclic 65 % *trans* polymer 18 and isomeric mixture of byproduct 29.

It is interesting to note that the geometric configuration of cyclic olefin produced by back biting is not determined by the geometry of the internal double

bond within the polymer from which it is formed, but instead depends upon the geometry of the alkylidene and the face of the internal olefin which initially attacks the metal. The geometric rotamers of a Schrock-type molybdenum alkylidene are defined in Figure 5.8.

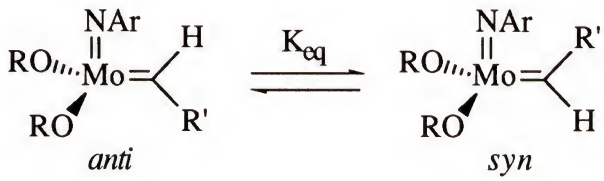


Figure 5.8. *Anti* and *syn* rotamers for a molybdenum alkylidene.

Syn and *anti* rotamers for both the W and Mo Schrock-type alkylidenes are defined by the orientation of the alkylidene substituent (R') in relation to the π-bonding ligand (NAr), and have been shown to interconvert at room temperature.[278] The equilibrium of the interconversion is greatly dependent upon the electron withdrawing strength of the alkoxide ligand and solvent conditions.[279] For the molybdenum catalyst (1c) used here, K_{eq} = 1450 (toluene, 25 °C) for the *anti* to *syn* interconversion, and the rate for this process decreases as the electron withdrawing power of the alkoxide ligand increases.[279] It has also been shown that the minor rotamer, *anti*-1c, is the more reactive toward the ring opening polymerization of norbornenes.[279]

Both *cis* and *trans* internal polymer olefins, as well as both *anti* and *syn* alkylidene rotamers can produce either the *cis* or the *trans* cyclotrisiloxalkene 29 (Figure 5.6). It seems reasonably and intuitively clear that the approach of the alkylidene to the olefin and the resulting geometry of the alkylidene/olefin complex dictates the stereochemistry of the cycloalkene back biting product. Figure 5.9 exhibits a simplistic illustration of the possible scenarios which can occur in order to produce a cycloalkene with a particular olefin stereochemistry.

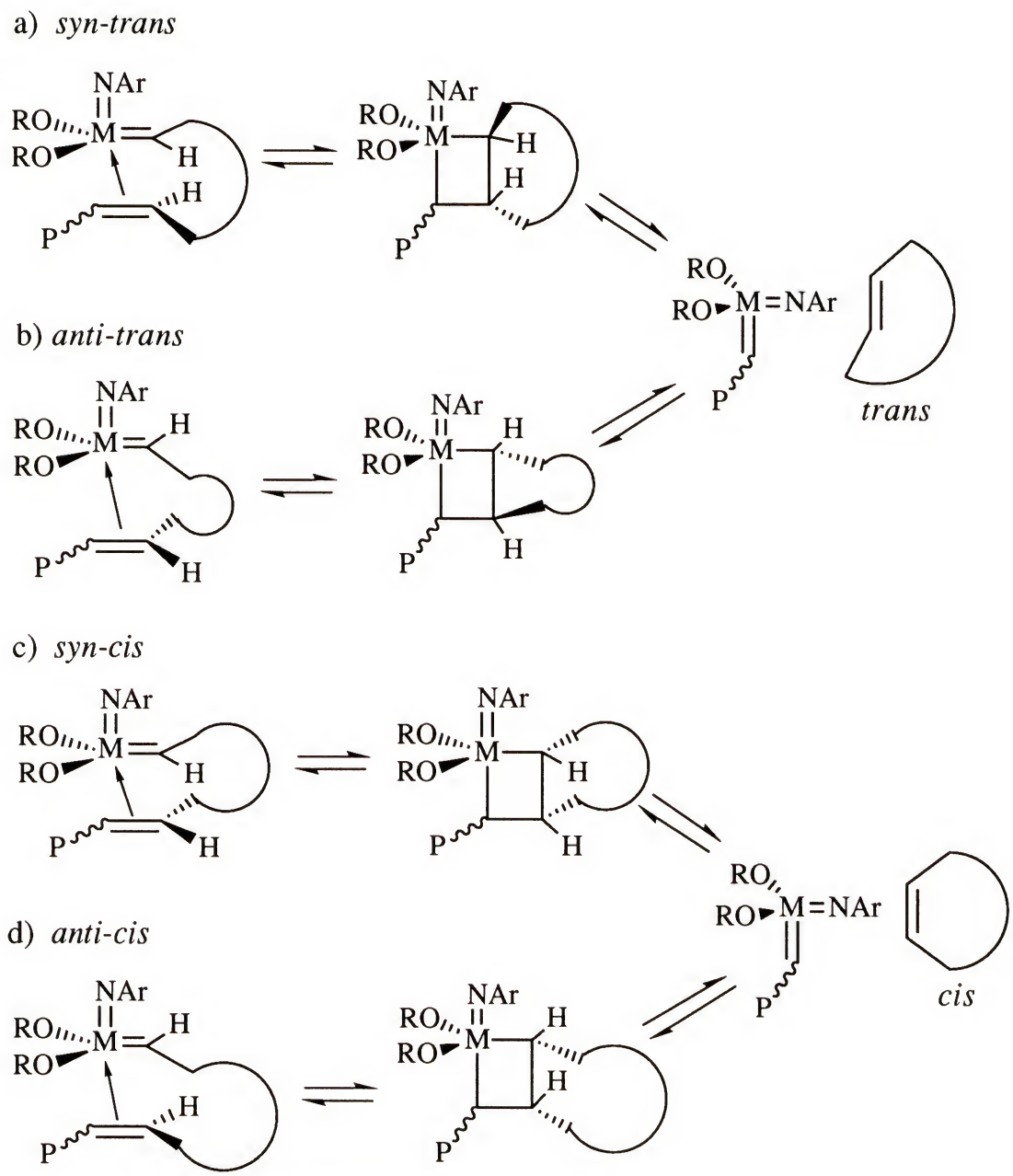


Figure 5.9. Generalized geometries for intermediates participating in back biting reactions, where M = Mo, R = $CMe(CF_3)_2$ and P = Polymer.

The back biting equilibria in Figure 5.9a-d can be loosely defined by the configuration of the alkylidene rotamer initially participating in back biting (*syn* or *anti*) and the relative stereochemistry of the metallabicycle formed (*trans* or *cis*), with respect <u>only</u> to the α,β disubstitution comprising the cyclic to be formed.

The true representation of this process is much more complex than indicated in Figure 5.9 and would require a tedious description of the many permutations derived from the three stereocenters in each trisubstituted metallacycle. Nevertheless, the relative geometry of the cycle forming substituents is sufficient for describing the formation of a *cis* or *trans* product.

The olefin is shown to attack on the C/N/O face of the alkylidene since this is considered to be the most favored approach.[280] The resulting metallabicycles will then contain a fixed relative substituent geometry dictated by the alkylidene rotamer, and, at least in part, by the approach of the internal olefin. The four possibilities indicate that the exact geometry of the internal polymer olefin need not be defined, however, it is unlikely that a tri-substituted metallacycle would form where all the substituents were mutually *cis*.

Conclusions

Cyclization reactions which occur during ADMET polymerizations are the result of slow back biting reactions when cyclic products are favorable. Cyclic products are not observed until a postcondensation resting state equilibrium is attained. Only the kinetically favored cyclic byproducts containing one or two repeat units are formed, and oligocyclic products are not detected for the polycarbosilanes or polycarbosiloxanes described in Chapters 3 and 4, respectively.

Polycarbosilanes 4 and 6 formed trace amounts of cyclic products after ADMET condensation had ended, and the polymers had reached a resting state equilibrium. For poly(dimethylsilabutenylene) (4), the 10-membered *cis,cis* cyclic repeat unit dimer was favored over the 5-membered single repeat unit product.

Polycarbosilane (6), possessing an 8-membered repeat unit produced the back biting product containing a single repeat unit.

Polycarbosiloxane 18 underwent back biting at the postcondensation resting state where a ring/chain equilibrium was observed. The 9-membered trisiloxalkene could be generated in the bulk by its continuous removal, or to a greater extent, by diluting active polymer 18. Dilution favored the production of the back biting product by slowing all other inter-chain equilibria. Both geometric isomers of the 9-membered cyclotrisiloxalkene were isolated, the extent of which depended upon the ability for metathesis mediated isomerization of the formed cycloalkene and not the configuration of the polymer olefin.

CHAPTER 6

CONTROLLED DIENE INSERTION IN POLY(TRISILOXABUTENYLENE)

Chapters 3 and 4 presented the design and synthesis of unsaturated silicon containing polymers where specific monomer structural relationships were confronted. The ADMET polymerization of acyclic carbosiloxadienes using the molybdenum analog of Schrock's catalyst 1c (Figure 4.1) created a new class of polycarbosiloxanes containing regular alternations of alkenylene linkages. These unsaturated siloxane polymers complement the synthetic emphasis devoted to organofunctional polysiloxanes, polymers which are important due to their unique combination of valuable properties, as described earlier.[11,19,20,31] In particular, polycarbosiloxanes containing aromatic linkages possess advantages over traditional siloxane polymers and are, for the most part, currently confined to the condensation of bis(silanol)benzenes with dihalosilanes.[38,43-46] These condensation techniques are typically accompanied by redistribution reactions where polymer regularity is seldom achieved, as discussed in Chapter 1 (Figure 1.4).

Previous attempts (in Chapters 3 and 4) toward the synthesis of high molecular weight silicon polymers containing aromatic groups via ADMET chemistry were met with limited success due to synthetic difficulties. The aromatic carbosiladiene (8) and carbosiloxadiene (22) used in Chapters 3 and 4, respectively, produced only low molecular weight polymers when using either the tungsten based (1b) or the molybdenum based (1c) catalysts. These results

directed the research described in this Chapter to the alternative route of accessing aromatic containing polycarbosiloxanes via ADMET copolymerization. The co-condensation of a small molecule aromatic diene with an unsaturated polycarbosiloxane was chosen as a method of obtaining aromatic linkages within the polymer. In this work, the alkylidene catalyst 1b (Figure 6.1) was chosen since there exists evidence that the tungsten catalyst is more reactive, than is the molybdenum analog, toward internal olefins .[185]

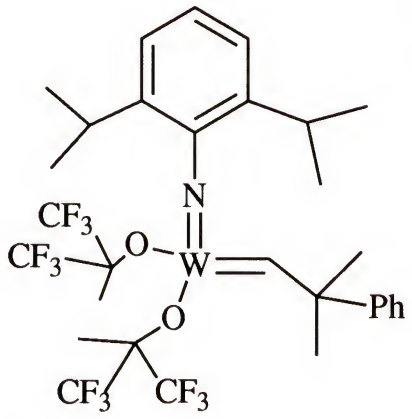


Figure 6.1. Lewis acid free alkylidene catalyst 1b.

ADMET polymerization is a very versatile method of constructing unsaturated copolymers since the equilibrium condensation mechanism is not monomer property (such as ring strain) dependent, thus allowing for an indiscriminate co-condensation between different dienes. Other ADMET researchers have demonstrated, using neopentylidene catalyst 1a, that the bulk copolymerization of two different dienes, or the bulk copolymerization of an unsaturated polymer with a diene monomer, results in random copolymers containing all possible linkages.[236] It has also been shown that if unsaturated polymer is co-metathesized with excess monoene, then spontaneous depolymerization occurs producing well defined monoene terminated oligomers.[245]

In ADMET chemistry, the alkylidene catalyst, 1b (Figure 6.1), establishes an equilibrium between molecules containing metathesizable sites of unsaturation, regardless of olefin concentration in each reactant. Degenerate inter-chain metathesis is known to occur in ADMET polymerizations where *trans* olefin geometry increases with extent of reaction.[232,235] While random copolymers are produced under bulk conditions, the slow addition of comonomer in solution to an existing unsaturated polymer was predicted to offer more than statistical control of monomer insertion. In this Chapter, an extension of ADMET copolymerization is presented, when using catalyst 1b, by demonstrating the facile single repeat unit insertion of a small molecule aromatic diene into an unsaturated polycarbosiloxane.

Monomer/Polymer Copolymerization

The reaction of a dilute solution of 4,4'-bis(*trans*-1-propenyl)biphenyl (30) (Figure 6.2) with α,ω-diallyl-poly(hexamethyltrisiloxabutenylene) (18) was predicted to yield a copolymer (31) with isolated linkages of the added diene. The simple idea of constructing the linkages desired in excess, prior to addition of the comonomer, 30, reduces the probability of structural irregularities such as dimerization of diene 30. The bulk copolymerization of 1,4-dipropenylbenzene and 1,9-decadiene has been reported by other ADMET researchers where dimerization of the aromatic diene was found to be favored over a statistical distribution of copolymer linkages resulting in block-type structures.[237] As will be shown, ADMET chemistry can allow control over copolymer structures when appropriate conditions are employed. Figure 6.2 illustrates the copolymerization reaction scheme.

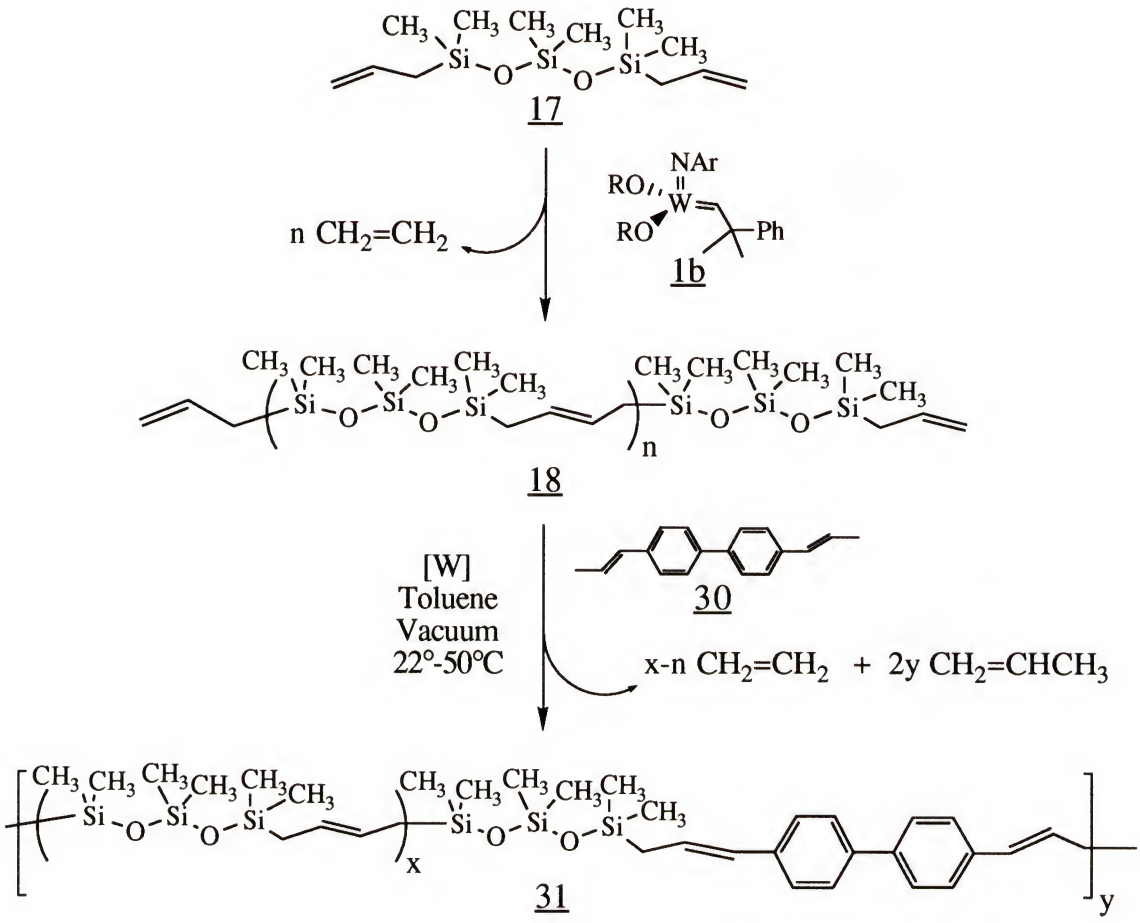


Figure 6.2. Synthesis of copolymer 31 containing isolated aromatic units.

The homopolymerization of monomer 17 to polymer 18 was described in Chapter 4 using the molybdenum catalyst 1c. Here, tungsten catalyst 1b was used to oligomerize carbosiloxadiene 17 in preparation for the inter-chain co-condensation of 18 with monomer 30. Although the polymerization was purposely slowed (by increasing the pressure of the reaction) before high polymer 18 was obtained, high molecular weight polymer 18 is easily achieved with longer reaction times under reduced pressure when using catalyst 1b or the molybdenum analog as described in Chapter 4.

Prior to copolymerization, polycarbotrisiloxane 18 was sampled for analysis and was found to possess an average M_n = 7650 (DP~30) as determined by

quantitative ^{13}C NMR endgroup analysis and a M_w/M_n = 1.7 vs. polybutadiene standards. The butenylene linkages in polymer 18 contained an average 67 % *trans* geometry by quantitative ^{13}C NMR, which is typical for ADMET polymerizations limited by reaction time.[232,252] Since bulk ADMET polycondensation, catalyzed by 1b, produces structurally pure and linear polymers void of contaminating byproducts, polymer 18 possessed well defined sites of unsaturation. These sites are further reactive toward continued metathesis condensation, and therefore polymer 18 did not require isolation or purification.

The viscous liquid nature and excellent solubility of unsaturated polycarbosiloxane 18 designated it as an attractive candidate for the co-metathesis condensation with the very rigid small molecule diene, 4,4'-bis(*trans*-1-propenyl)biphenyl (30). ADMET polymerization is not compatible with the required conditions for homopolymerizing diene 30 to form poly(biphenylenevinylene). For example, an insoluble solid was produced within minutes when attempting to homo-condense diene 30 by treatment with catalyst 1b in toluene. Only the partially soluble ADMET dimer of 30 was confirmed by ^{1}H NMR spectroscopy. The trisiloxane linkage in polymer 18 features two Si-O-Si linkages per repeat unit which impart excellent solubility and low temperature flexibility to the backbone as indicated by the extremely low glass transition temperature (T_g = -97 °C) measured for high molecular weight 18, as discussed in Chapter 4 (Figure 4.16).

The slow and dilute addition of aromatic diene 30 (0.1 M) to polymer 18, in the presence of active Schrock's catalyst (denoted as [W] in Figure 6.2), resulted in the isolated incorporation of the biphenylene linkage. Resonances indicative of diene 30 dimerization, i.e., stilbene signals, were not detected in the ^{1}H or ^{13}C NMR spectra for copolymer 31 at 200 MHz and 50 MHz, respectively (Figure 6.3). Furthermore, NMR analysis of the copolymer revealed that propagation

proceeded to the extent that the molar concentration of terminal endgroups fell below the limit of detection for NMR endgroup analysis (see Figure 6.3). Terminal vinyl carbon signals present in polymer 18 are easily resolved in the ^{13}C NMR spectra yet are absent in copolymer 31. Clearly, in addition to incorporation of the aromatic diene 30 into polymer 18, terminal olefin condensation also continued and the molecular weight increased substantially.

Figure 6.3 also displays the ^{13}C NMR spectra for the aromatic diene 30. Every nonequivalent carbon was identified in the copolymer based on the easily assigned carbon signals for polymer 18 and biphenyldiene 30. The average *trans* geometric isomer content of the butenylene linkages contained in the copolymer increased only slightly to 70 % *trans* (from 67 % for 18), whereas only one geometric isomer for the biphenylene connections was detected by ^{1}H and ^{13}C NMR spectroscopy at 200 MHz and 50 MHz, respectively. Comparison of the three spectra in Figure 6.3 shows conclusively that single repeat unit insertion of diene 30 was achieved. Resonances corresponding to the propenyl carbons in 30 (signals 1, 2, and 5 in center spectrum) are absent in the ^{13}C NMR spectrum for the copolymer, and new resonances for the vinylic (signal 10, lower spectrum) and allylic (signal 5 same) carbons connecting the aromatic ring of 30 to the allylsilane carbon of 18 appear. The vinylic carbon, β to the aromatic *ipso* carbon, however, is not resolved in the NMR spectrum for copolymer 31 and is most likely contained within one of the aromatic signals.

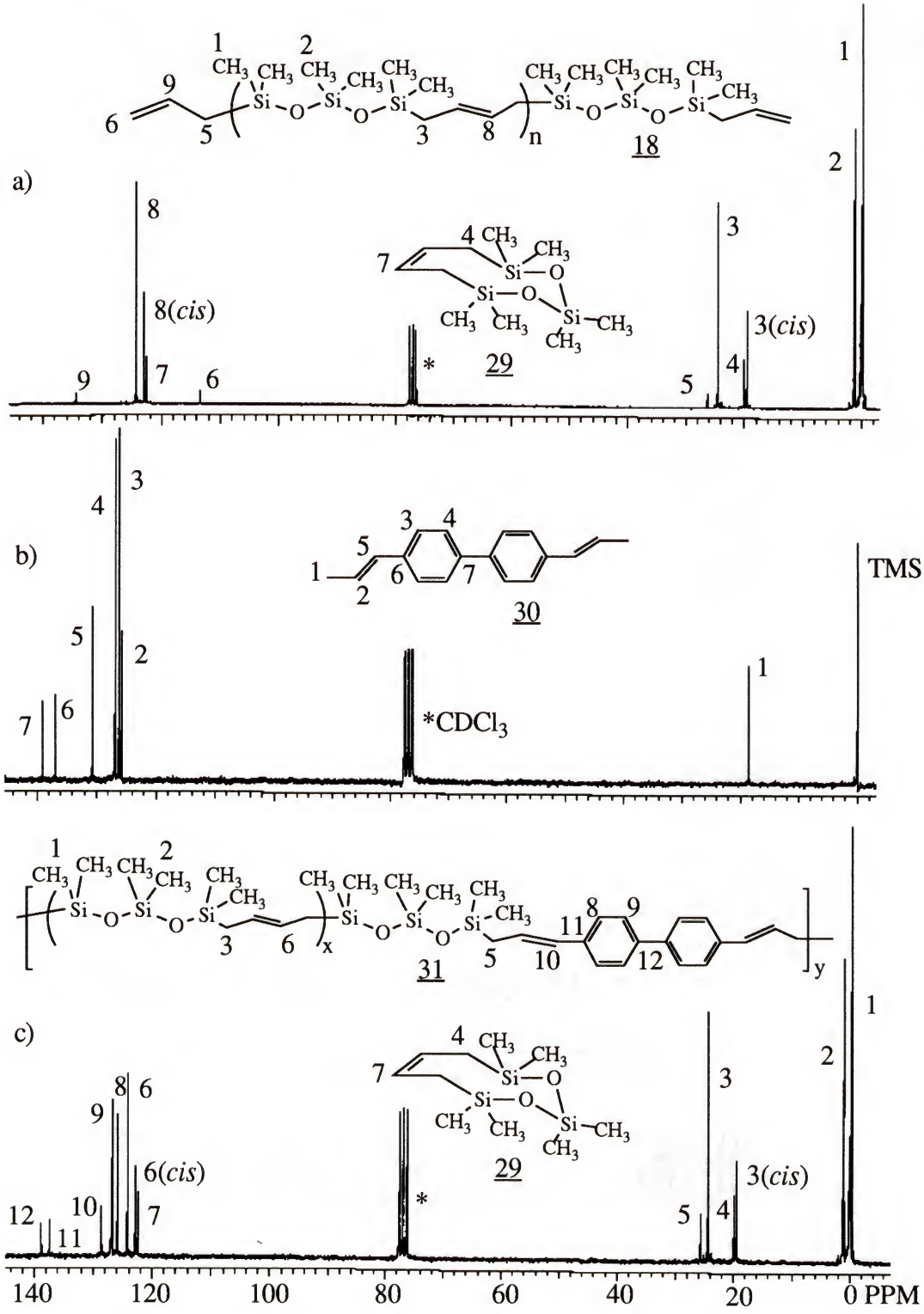


Figure 6.3. 50 MHz ^{13}C NMR spectra of a) 67 % *trans* polymer 18, b) aromatic diene 30, and c) 70 % *trans* copolymer 31.

The ^{13}C NMR spectra in Figure 6.3 also indicate that metathesis backbiting reactions occurred when polymer 18 was diluted, as described in Chapter 5 (Figure 5.6). Carbon signals at 20.3 ppm (signal 4) and 121.3 ppm (signal 7) found in both spectra for the homopolymer 18 and copolymer 31, correspond to the allylic and vinylic carbons, respectively, of the 9-membered cyclic, hexamethyltrisiloxanon-7-ene (29). Only the *cis* isomer is formed in solution, whereas the *trans* isomer of this cyclic backbiting product from polymer 18 was also isolated from the bulk, as detailed in Chapter 5 (Figure 5.6). Quantitative ^{13}C NMR revealed that 11 mol% cyclics formed upon initial dilution of polymer 18, and this quantity did not significantly change throughout the copolymerization. Ring/chain equilibrium is rapidly obtained for active polymer 18 in solution where the extent of cyclization is dependent upon the relative concentrations of the polymer and cyclic product. As demonstrated in Chapter 5, cyclosiloxalkene 29 has been produced in greater concentrations (36 mol%) for more dilute solutions.

Analysis by GPC further supports copolymer formation by exhibiting a monomodal distribution representing an average M_n = 29000 (relative to polybutadiene standards) and M_w/M_n = 1.9 as predicted for step condensation polymerizations (see Figure 6.4). The aromatic diene 30 was not detected by GPC analysis of the copolymer (31) reaction mixture. This evidence indicates that essentially quantitative insertion of diene 30 into polymer 18 was achieved. Integration of the aromatic signals in the ^{1}H and ^{13}C NMR spectra vs. the butenylene signals also suggests that the degree of incorporation of the biphenylene unit into polymer 18 was quantitative. Figure 6.4 also contains the GPC trace for the ambient degradation products formed from copolymer 31 and is discussed in later sections.

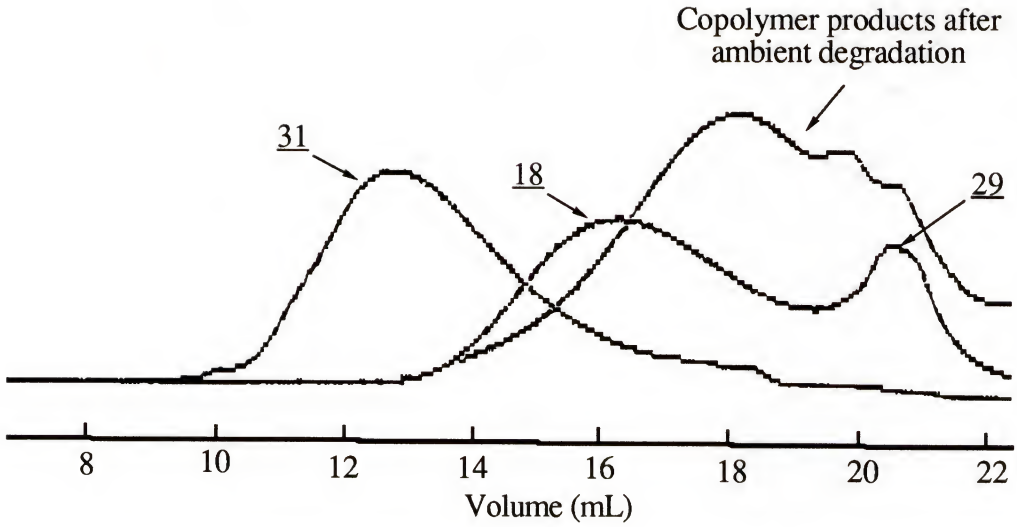


Figure 6.4. Gel permeation chromatography (GPC) of a) polymer 18, b) copolymer 31, and c) ambient degradation products of 31.

The copolymer was examined further by UV spectroscopy, and its spectrum was compared to that of aromatic diene 30, as illustrated in Figure 6.5. Pure 4,4'-bis(*trans*-1-propenyl)biphenyl (30) exhibits a λ_{max} = 306 nm (ε = 50600 $cm^{-1}mol^{-1}L$) compared to a λ_{max} = 317 nm for the copolymer. The slight bathochromic shift in λ_{max} for the copolymer is expected due to electronic perturbations[27] from the allylic silicon atoms in the copolymer. Allylsilane perturbation, or hyperconjugation, derived from the "β-donor-effect" is well known in organic chemistry due to the reactivity of allylsilanes toward electrophiles.[15] This shift in the copolymer absorbance cannot be attributed to biphenylene dimerization, which results in a significantly more conjugated stilbene linkage. For example, the model compound 4,4'-diphenylstilbene exhibits a λ_{max} = 360 nm.[280] Pure homopolymer 18 exhibits a weak absorbance in the UV with a λ_{max} = 312 and is not resolved in the copolymer due to the strong absorbing biphenylene linkages. Although the shoulder near 360 nm for the copolymer is indicative of trace dimerization of the biphenylene monomer, these linkages are not observed in the NMR spectrum (Figure 6.3).

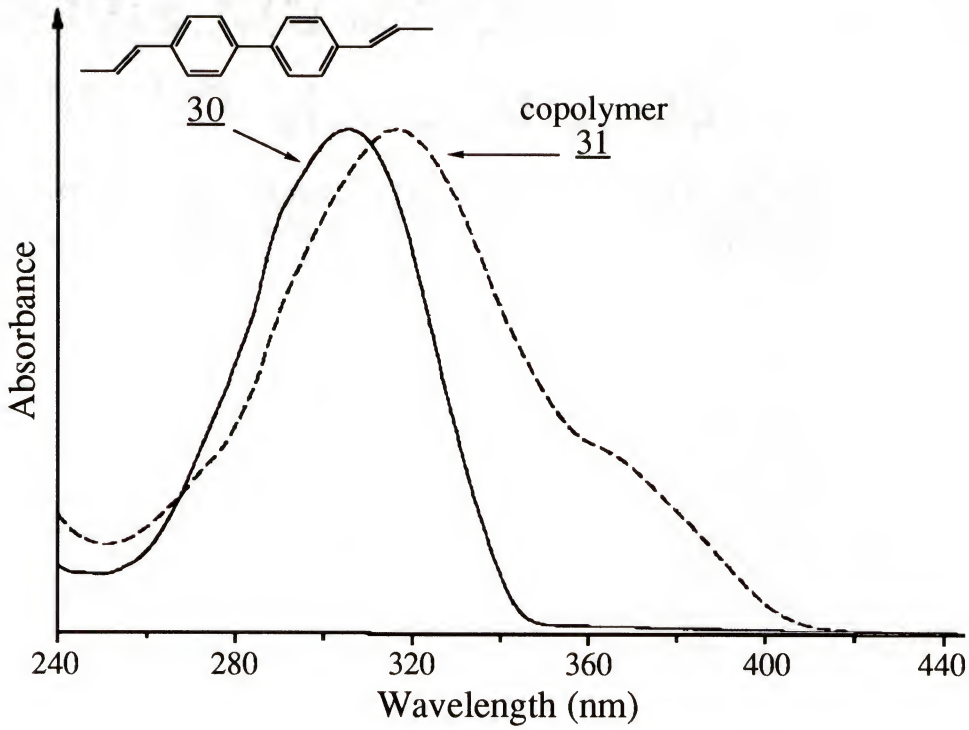


Figure 6.5. UV spectra of biphenylene diene 30 and copolymer 31 (in THF).

Copolymer Thermal Stability and Reactivity

The thermal stability and extent of decomposition of copolymer 31 and polymer 18 are compared in Figure 6.6. The thermal stability of polymer 18 in nitrogen is only slightly improved by the incorporation of the biphenylene linkages. Some weight loss begins below 200 °C for the oligomer, and at 377 °C (10 % weight loss), rapid decomposition ensues for 18 compared to 420 °C (10 % loss) for the copolymer. The copolymer decomposes to a maximum 90 % of its original weight at 579 °C, whereas 18 loses 100 % of its weight at 500 °C.

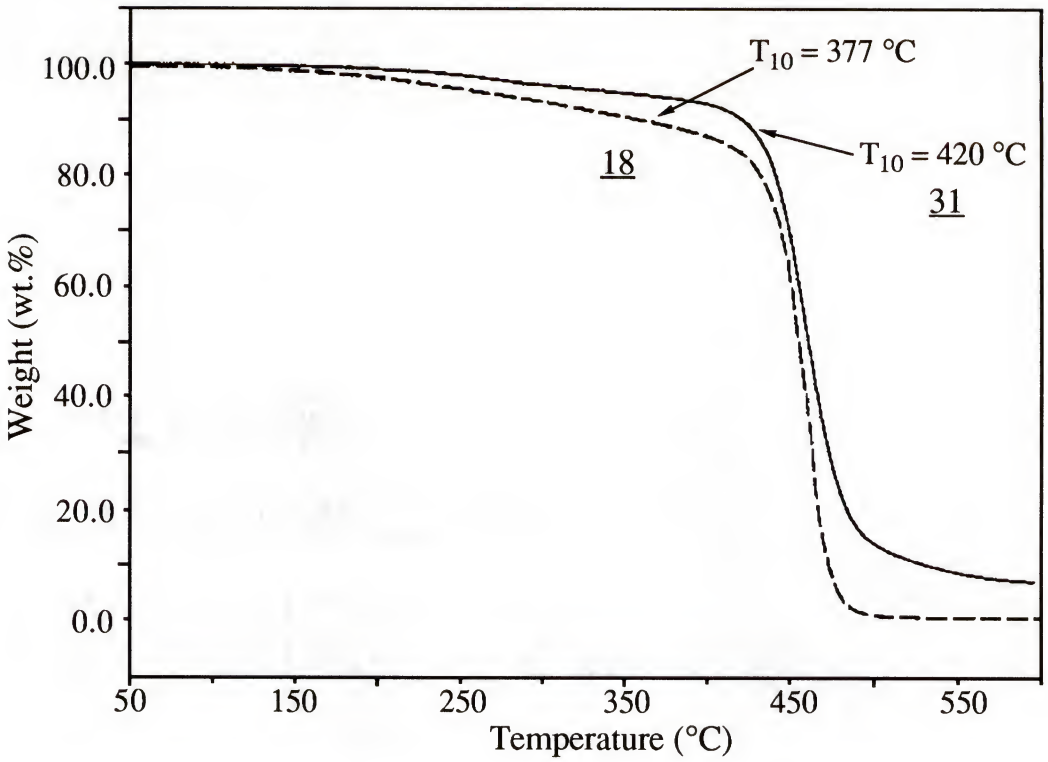


Figure 6.6. Thermogravimetric analysis (TGA) of polymer 18 and copolymer 31 in N_2: scan rate 10 °C/min.

Copolymer 31 also underwent uninitiated cross linking under an inert and otherwise ambient atmosphere ($\lambda > 400$ nm). After standing at room temperature under argon for several days, copolymer 31 became a low integrity rubbery film which was insoluble in THF. The cross linking is light, however, as indicated by swelling copolymer 31 in THF; where after 24 h, 80 % extractables were obtained. Presumably, the chromophoric biphenylene linkages sensitize photo cross linking since the trisiloxane homopolymer, 18, does not undergo cross linking and is, in fact, stable indefinitely under ambient conditions.

Copolymer 31 further degraded to lower molecular weight products after prolonged standing in air. Previously cross linked copolymer 31 returned to an oily state and became mostly soluble (~ 95 %) immediately without swelling in THF. Analysis of the degraded product by GPC revealed various oligomers

representing a substantial decrease in molecular weight (Figure 6.4). Thermal gravimetric analysis of the air exposed product (Figure 6.7) exhibited a much greater loss in thermal stability where consistent weight loss began at 150° C (10 % wt. loss at 208 °C). Presumably, the biphenylene induced photo cross linking that is prevalent under an inert atmosphere is accelerated in air to the point of degradation since homopolymer 18 is completely stable under prolonged exposure to air.

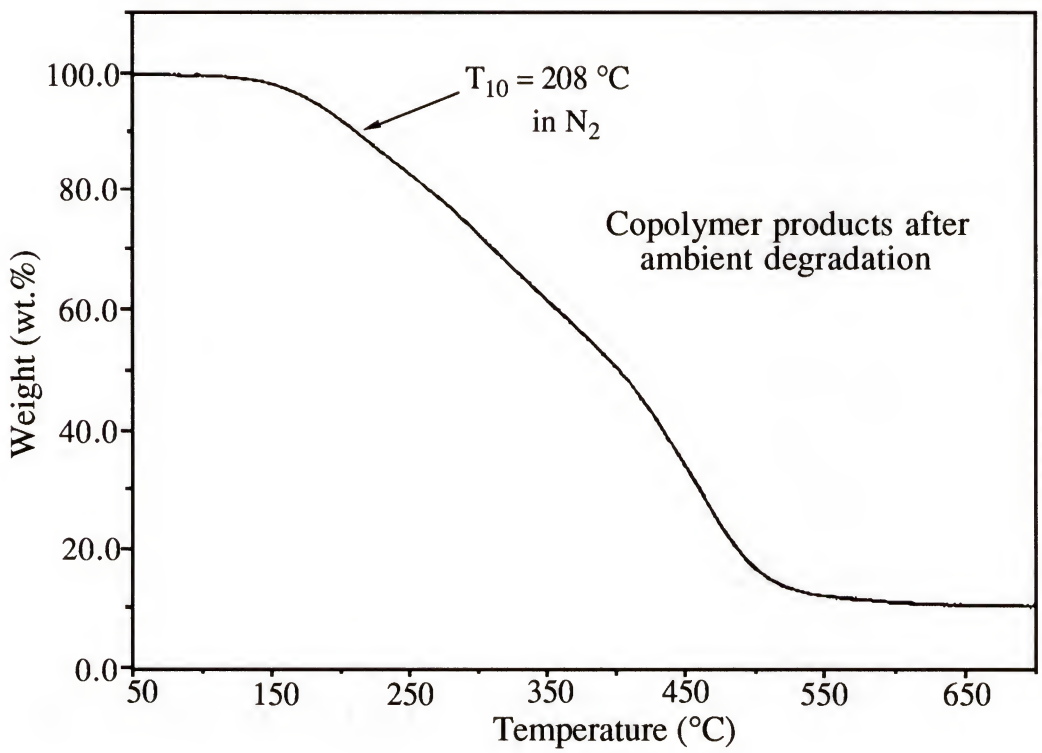


Figure 6.7 Thermogravimetric analysis (TGA) of copolymer 31 products after ambient degradation in N_2: scan rate 10 °C/min.

Conclusions

Single repeat unit insertion of an aromatic diene into an unsaturated poly(carbosiloxane) was achieved by the co-metathesis condensation of an

aromatic diene with an unsaturated polymer. The molecular weight of the copolymer was significantly increased (vs. the homopolymer starting material) during co-metathesis due to continued metathesis condensation of terminal olefins. Characterization of the copolymer by NMR and UV spectroscopy, and GPC suggests that the biphenylene units were predominantly isolated. The copolymer exhibited only a slight enhancement in thermal stability from the homopolymer and unlike the homopolymer, underwent uninitiated cross linking under an inert atmosphere. The copolymer further degraded after prolonged exposure under ambient conditions.

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BIOGRAPHICAL SKETCH

Dennis W. Smith, Jr., was born on December 15, 1965, in Atlanta, Georgia. At the age of nine he moved with his sister, Kim, and mother, Margaret, to Kansas City, Missouri, and then later to Camdenton, Missouri at the beautiful Lake of the Ozarks. He began his undergraduate career in 1983 at Southwest Missouri State University (SMSU) in Springfield, Missouri. His undergraduate work at SMSU consisted of epoxyeneone syntheses and mechanisms under Dr. Tamera Jahnke for which he received the Dow Chemical Undergraduate Research award in 1984. He later worked as a student cooperative employee for Dayco Corporation in the area of polymer property testing and then for the SMSU Center for Scientific Research where he explored the design and synthesis of novel polyamide imides. He began his graduate studies at the University of Florida chemistry department, within the division of organic chemistry, in January, 1989, after receiving a B.S. degree in chemistry and mathematics. His graduate research was directed by Professor Ken Wagener and included a 4 month research mission to Lyon, France, where he worked for Rhone-Poulenc in the area of silicone technology. Upon receipt of his Ph.D. in December, 1992, he began a career with the Dow Chemical Company under the research assignments program beginning with a one year postdoctoral fellowship at Dow Deutschland in Rheinmünster, Germany.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kenneth B. Wagener, Chairman
Professor of Chemistry

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James M. Boncella
Associate Professor of Chemistry

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William R. Dolbier, Jr.
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Merle A. Battiste
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Eugene P. Goldberg
Professor of Material Science
and Engineering

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1992

Dean, Graduate School